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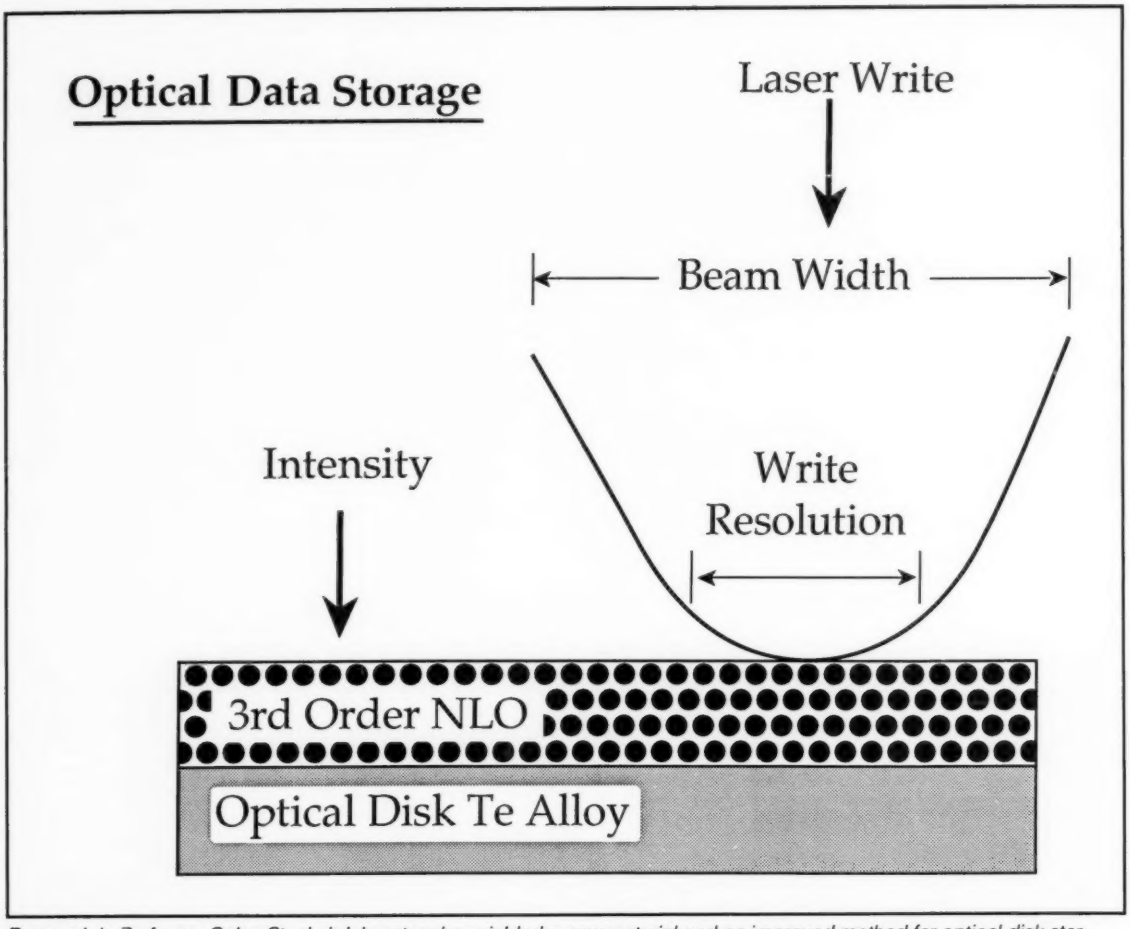
CLUSTER SCIENCE



Research in Professor Galen Stucky's laboratory has yielded a new material and an improved method for optical disk storage. This figure is a schematic diagram of the process of laser "writing" on an optical disk storage medium. In order to get the highest resolution, the laser is focused as tightly as possible. However, the optical density will be limited by diffraction effects at small laser beam diameters and by the inhomogeneity of the laser intensity in its cross section, which also restricts the sharpness of reproduction. ONR-sponsored research contributed to the development of a new optical medium material that consists of quantum confined semiconductor clusters, which have nonlinear optical (NLO) properties. These properties include the variation of the refractive index and absorption edge with laser intensity, yielding an optical transistor. In essence, using a nonlinear optical material coating allows only the center portion of the laser beam, which has an intensity above a particular threshold, to be selected, which dramatically improves optical density, resolution and recording quality (see article by Stucky in this issue.)

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About the Cover

The figure on the front cover shows the C_{82} fullerene with a lanthanum atom inside of the cage. The C_{82} structure is that predicted by quantum mechanical calculations of Fowler and Manolopoulos. This LA@C_{82} species was produced in Professor Richard Smalley's laboratory and is the first internally-doped fullerene, or endohedral complex, to be generated in macroscopic quantity (see article by Smalley in this issue.)

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Introduction

Mark M. Ross

Chemistry Division, Office of Naval Research

Clusters represent the transitional "phase" of matter between the individual atom of a particular element and the bulk solid state. While monitoring cluster properties as a function of size is important in following this transition, the majority of the efforts in this field is motivated by curiosity about the fundamental aspects of clusters, as unique and interesting species in and of themselves, as well as by the great potential that clusters offer as new materials. In order to realize this potential, researchers have focused on obtaining a better understanding of cluster formation, cluster structures and cluster properties. The research has spanned a broad range of scientific disciplines: from studies of the physical chemistry of isolated, gas-phase clusters to those of the solid-state properties of bulk, cluster-based materials.

The ONR Accelerated Research Initiative on cluster science was formulated in 1986 because of the opportunities for research on clusters and sought to bring together an interdisciplinary scientific effort to focus on advancing the knowledge of these novel pieces of matter. The following four articles, which focus on the chemistry portion of the program, provide strong evidence for the success of this ARI. In addition to exciting and unexpected results, this program has produced several collaborations between scientists of different expertise that may not have occurred otherwise. Some of the many significant accomplishments of the research supported by the ARI are described in these articles, which report the state of the art as well as future directions in cluster science.

In the first paper, Professor Richard Smalley describes what is now the prime example of basic research on clusters leading directly to new materials. Six years ago the number of experimental research groups studying carbon clusters (as we once called them) could be counted on one hand. Observation and characterization of the properties of the supreme "magic number" cluster of 60 carbon atoms have resulted in a new form of carbon. While most of us know that cluster research is important, few if any could have predicted the present state of activity on fullerenes. It is important to emphasize that gas-phase studies provided, and continue to yield, much of the crucial information and motivation for this new area of science. Here, Prof. Smalley focuses on the recent efforts to dope fullerenes with metal atoms in attempts to produce and characterize another new class of material. His work continues to provide exciting new insights and opportunities in cluster research.

The second article, by Professor John Weaver, takes clusters from the gas phase onto surfaces. For a long time, clusters have been speculated to be important in nucleation and growth of films. This paper describes methodical studies aimed at understanding thin film formation using atomic versus cluster precursors. Prof. Weaver has developed a new approach to forming and using clusters for production of metal overlayers on various substrates. His cluster assembly technique avoids many undesirable aspects of atom deposition and provides a general method for producing films with abrupt interfaces. His research on the fundamental aspects of cluster/surface interactions has yielded a unique and technologically-important application of clusters.

In the third article, Professor Galen Stucky shows the utility of clusters in the solid-state as he describes his research on cluster-based materials. His work has focused on the critical issue of how to "package" clusters, which have desirable properties, in a framework that yields a usable material. He has developed host/guest solid-state chemical methods to incorporate semiconductor clusters into three-dimensional solid matrices. The resulting nanocomposites can provide some advantageous optical properties. One application of such materials developed in this research is described on the inside cover of this issue.

In the fourth and final paper, Dr. Brett Dunlap presents an overview of research performed in the Chemistry Division of the Naval Research Laboratory in the cluster chemistry program, which has been an active area since 1980. While many types of clusters have been studied during the course of this program, C_{60}, as well as related fullerenes and fullerene derivatives, are emphasized in terms of the detailed insights on cluster properties that can be gained through use of total energy density functional (theoretical chemistry) methods.

These articles provide excellent examples of exciting and important cluster research. This field is increasing in activity as knowledge of clusters advances. In addition, the research described in this issue shows that the potential of clusters as new materials, which has been discussed for a long time, is now being realized. It is clear that fundamental research on clusters has yielded numerous important discoveries, in the way of new materials and new areas of science. It is equally obvious that basic research must continue in order to achieve the full promise that clusters offer.

The Third Form of Carbon

Richard E. Smalley
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Introduction

In chemistry class in high school, most of us can remember hearing for the first time of one of the most vivid examples of chemical change. The pencil in our hands, we were told, contained elemental carbon in the form of graphite. As we dragged this pencil across a white page of paper, the black line left behind was, apparently, just a trail of carbon. In fact all the writing in most every book we'd ever read was, we were told, made from carbon black – a nearly pure form of graphitic carbon. Here the individual carbon atoms were attached to each other to form hexagonal rings, and these rings were joined with other hexagonal rings, producing a two dimensional sheet of hexagons – like a huge sheet of chicken wire. The black typeface characters one sees on the typical printed page are composed of thousands of tiny black graphite particles, each containing many such chicken wire sheets stacked one atop another.

But we were then told there is a second form of pure carbon, one where the carbon atoms are connected in a tetrahedral lattice. If the common, dirty-looking graphite is simply pressed hard enough at a very high temperature, the chemical bonds can be rearranged so that the material is converted into this strikingly different form of carbon – it is converted into diamonds. This hard, smooth, brilliantly refractive gem stone, also familiar in our youthful experience from many touches of our mother's wedding or engagement ring, seemed so totally alien from sooty graphite that it was hard to believe the chemistry professor's claim that it was composed of just the same old carbon atoms. We were told that this equivalence could be proven simply by burning the diamond in oxygen and demonstrating that the only product was just CO_2. And not a few of us wondered if we had the guts to actually burn one to find out!

Knowledge of these two crystalline forms of pure carbon dates back into the mists of prehistory. To be sure, modern chemistry and materials science has developed other forms of carbon which appear at least superficially to be different, e.g., amorphous carbon, carbon fibers, diamond-like films, and various forms of carbon/carbon composites. But all of these can be understood as mixtures of small domains of graphite or diamond with varying degrees of bonding disorder. They do not constitute distinct allotropes of carbon. There are only two stable ways of arranging carbon atoms alone into a perfect, pure crystalline form: graphite and diamond.

At least this is what we were all told. Given the fact that no other form has been identified for many thousands of years, and the fact that carbon has been the most-studied of any element since the dawn of chemistry this situation seemed unlikely to change.

But is has.

As a result of fundamental research over the past six years, it is now clear that this old story about the two forms of carbon is in for a rather major update: now there are THREE forms of pure carbon. We just found a new one.[1]

Fullerenes - A Molecular Form of Pure Carbon

The new form of carbon is actually more of a new class of forms than a single entity. Unlike the first two, graphite and diamond, which are infinite periodic network solids, this third form of carbon is molecular. While there are an infinite number of possible variations, all members of this new molecular class share one property in common: they are hollow, geodesic spheroids, as shown in Figure 1. As a class they have been named "the fullerenes" after Richard Buckminster Fuller.

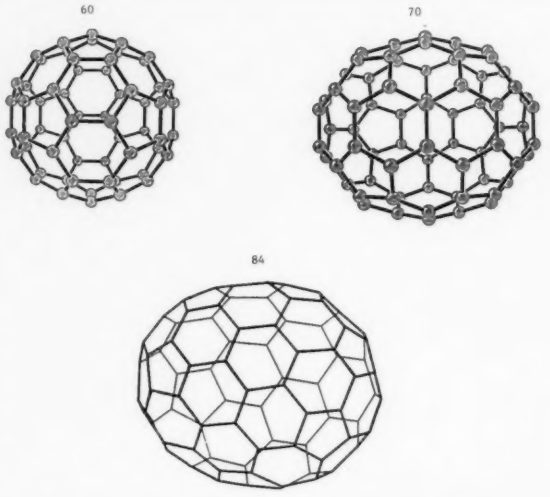
Fuller was an inventor, architect, poet, and philosopher of a uniquely American mold. Although his closest followers and students remember him most as a teacher and as a supremely independent and wide ranging philosopher, he is most widely known for his invention and advocacy of the geodesic dome. This structure which Fuller argued to be the most efficient means of enclosing space ever invented, was patented in the US in 1954 but first widely appreciated in the giant dome built for the 1967 Montreal Expo. The key architectural principle is that the dome is constructed of interlinked hexagons and pentagons made from tetrahedral subunits, with the pentagons arranged at what would be the corners of a perfect icosahedron (if the dome where continued all the way around to make a sphere). The result is that the stresses of the structure are distributed along the great circles – the geodesics – of the spherical dome, thereby giving it its great stability.

Unfortunately, R. Buckminster Fuller died in 1983. Had he lived only a few years later he would have been thrilled to learn of the discovery my colleagues and I made of the surprisingly stability of a series of even-numbered pure clusters of carbon, and of one cluster in particular, C_{60}. We rationalized this behavior could only have come about if the carbons had arranged themselves into tiny geodesic domes. In the case of the 60-atom cluster this dome took the perfect icosahedral symmetry of a soccerball, so we rather fancifully gave it the name "buckminsterfullerene," in honor of its architectural roots. Like benzene, naphthalene, and thousands of other aromatic molecules, carbon in this new geodesic form of carbon would be bonded to only three other atoms, the fourth valence of each carbon atom being satisfied in a strong double bond, delocalized over the geodesic sphere. But, unlike all previously known aromatic molecules, buckminsterfullerene, or "buckyball" as it was soon nicknamed did not involve hydrogen or any other element. The newly discovered molecule was just C_{60}, a pure, spherical form of carbon.[1-3]

The apparatus used to make this discovery is shown schematically in Figure 2. It was developed in the early 1980's as a general way of exploring what was then a brave new world for chemists, physicists and materials scientists: nanoscopic clusters – aggregates of atoms ranging in size from just 2 or 3 atoms, all the way up to many hundreds or thousands.[4] In this new apparatus these clusters were produced routinely for the first time from virtually any element in the periodic table by pulsed laser vaporization of an appropriate target material. For carbon cluster studies, a graphite disk was used for a target. It was rotated and translated under computer control so that successive shots of the vaporization laser traced out a spiral pattern, so that a fresh surface was hit each time. Using a 10-30 millijoule shot from the second harmonic of a Nd:YAG laser at 532 nm focussed to a 1mm spot on the target disk, vaporization temperatures exceeding 10,000 K were easily generated, so that even highly refractory elements such as carbon, platinum, or tungsten were readily vaporized.

Figure 1.

Selection of geodesic structures found to apply to the three most stable fullerenes: soccerball C_{60} (symmetry Ih), rugbyball C_{70} (symmetry D_{5h}), and chiralball C_{82} (symmetry D_2).



As shown in the figure, the laser-vaporized plume was entrained in a pulsed jet of helium, which served to cool down the vaporized atoms and aid in the formation of clusters. This cluster-laden pulse of helium was then allowed to expand through a supersonic nozzle, and the resultant supersonic free jet was skimmed to form a well-collimated supersonic beam in which the clusters were cooled and accelerated up to a uniform velocity.

The original result which led us to propose the buckminsterfullerene structure in 1985 came from such a supersonic carbon cluster beam. While measuring the mass spectrum of the clusters in the beam[2] we noticed that it was possible to vary the conditions in the laser-vaporization source so that the mass spectrum became increasingly dominated by C_{60}, and to a lesser extent C_{70}. Figure 3 shows some of these early results. As is evident in the top panel of this figure, where

conditions in the source were adjusted to maximize the time available for cluster reactions, C_{60} was found to be over 50 times more abundant than most other clusters in this size range.

In the field of clusters, such an effect is often called a "magic number" – a term brought over from nuclear physics – and there are many examples.[5] In the case of silicon and germanium clusters, for example, 10 is a specially stable cluster, as are those clusters with 21, 25, 33, 39, and 45 atoms.[6] But the sensational "magic" of the 60th cluster of carbon seen in the top panel of Figure 3 was at the time (and still is) completely unprecedented in cluster physics. It remains the all-time winner of the "magic number" sweepstakes.

The fact that it became increasingly special with increasing cluster chemical "cooking" in the supersonic nozzle suggested that somehow those clusters with exactly 60 atoms had been able to find a structure that eliminated dangling bonds, and did this with a perfection that no other cluster could match. At the time when we discovered how beautifully the soccerball structure explains this pattern it seemed reasonable to advance it as at least one interesting possibility. We couldn't think of another, but perhaps someone else would.

But over the intervening six years, even though this issue became one of the most controversial in chemistry, no one has ever been able to suggest an adequate alternative. The problem is how to explain the unique stability of C_{60}, the lesser but still substantial stability of C_{70}, and much smaller but significant chemical stability of all the even-numbered carbon clusters in this size range. In the soccerball explanation, this all comes about as a result of symmetry. The largest possible point group is the icosahedral group, I_h, which has 59 proper symmetry operations. This means that the largest number of atoms that can be arranged on the surface of a sphere such that each is interchanged with any other simply by a proper rotation is 60. In 3-dimensional Euclidean space there is no more symmetrical molecule possible.

The soccerball structure we proposed for buckminsterfullerene had this symmetry. Since it does the most perfect job possible of curling up a graphitic sheet so that no bonds dangle, and the strain of closure is evenly distributed, it is the least reactive of all possible carbon clusters. We knew that no alternative structural proposal for C_{60} could have this strong symmetry-based justification.

The other even-numbered carbon clusters were soon demonstrated to behave just as one would expect from a generalization of this geodesic dome motif. Fuller realized there were many variants possible for such domes, some not even very close to spherical, yet the stability and strength could still be maximized by using the interconnecting hexagons and pentagons. He knew the 18th century mathematician Leonard Euler had calculated that any such structure, if continued around to form a closed polyhedron, would have to have exactly 12 pentagons, though the number of hexagons could be increased as much as desired.

The soccerball structure we had hit on for C_{60} had 20 hexagons. With some fiddling we were able to find a similar structure for C_{70} that had an extra 5 hexagons arranged in a

Figure 2.

Laser vaporization supersonic cluster source used to produce the first fullerene molecular beams.

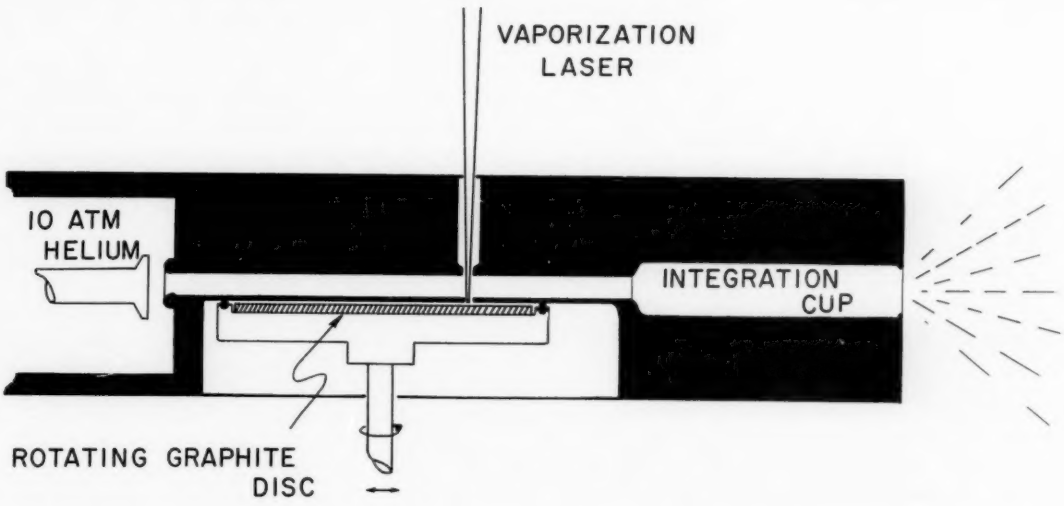
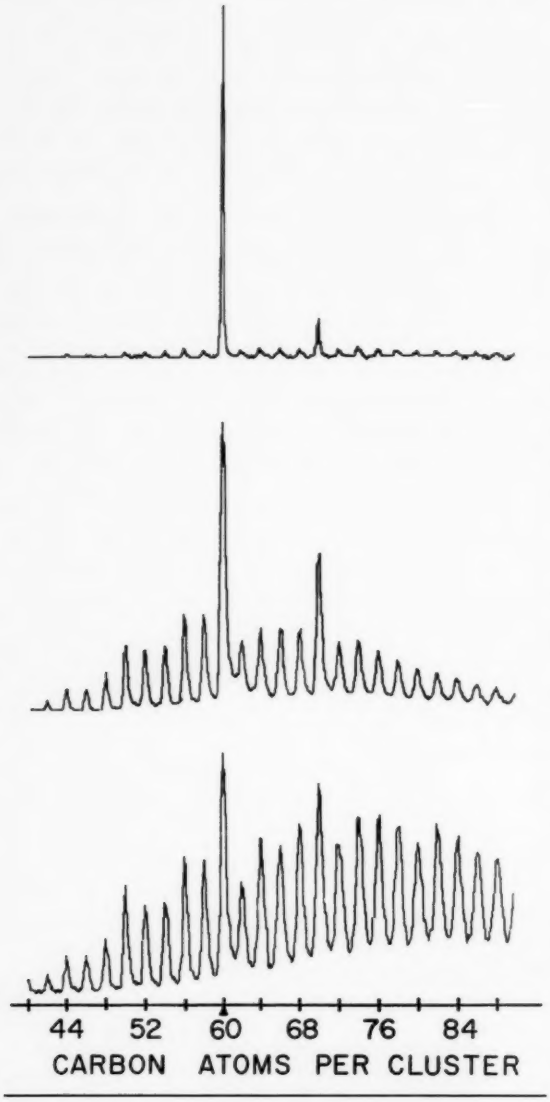


Figure 3.

Time of flight mass spectra of carbon clusters produced in a supersonic beam by the laser vaporization source of Fig. 2 adjusted to produce conditions of increasing cluster reactions (bottom to top).



belt smoothly connecting the two symmetrical hemispheres of C_{60}, producing a sort of rugby-ball shaped hollow cage. And with further work we were able to find at least one reasonable geodesic cage structure for each of the observed even-number fullerenes. In an obvious generalization of our rather unwieldy name for C_{60}, we suggested this entire class of geodesic cage molecules made out of 12 five-membered rings and any number of six-membered rings be termed fullerenes.

The name could hardly be more appropriate, for each of these molecules is itself a tiny, hollow geodesic dome, just as Fuller would have designed it if he worked on nanometer-sized construction projects.

Bulk Production of Fullerenes

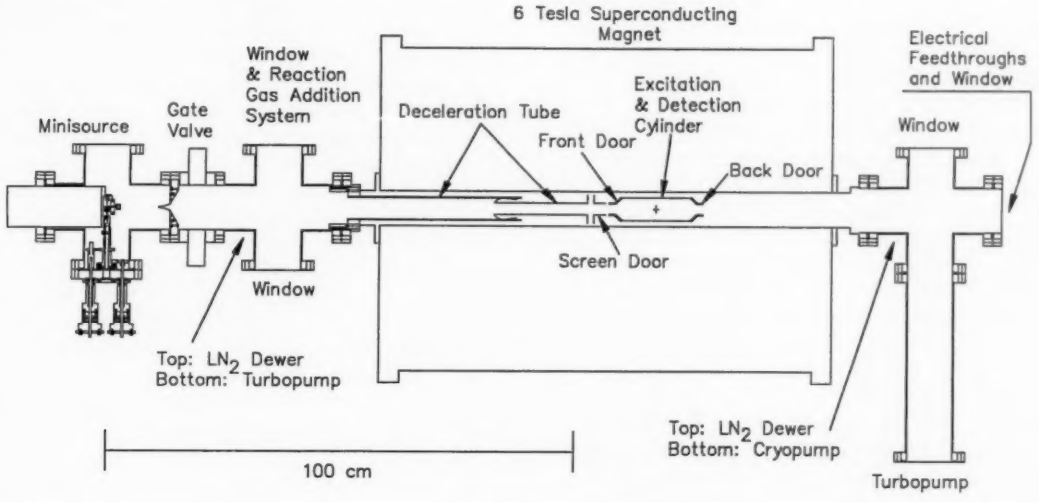
After the initial publication of our suggestion of the soccerball hypothesis for C_{60}, extensive other experiments and calculations were performed to test whether the suggested fullerenes were in fact being produced.[7,8] The special stability of the even-numbered fullerenes was verified for all charge states.[9-10] The ultraviolet photoelectron spectrum of the negative ion of C_{60} was shown[11,12] to be in detailed accord with calculations of the electronic energy levels expected for the icosahedral geodesic structure. Most strikingly, the large even-numbered clusters were shown to fragment by a bizarre mechanism where successive C_2 units "evaporated" out of the closed surface of the fullerene cage, causing it to shrink to form the next smaller fullerene.[13] This process was shown to continue until abruptly at C_{32} the strains of the surface curvature became too great, and subsequent laser excitation caused the cage to shatter. In 1988 this laser shrinking process was used to demonstrate that metal atoms could be trapped inside the cage.[14] With an internal potassium ion, for example, the fullerene cage was shown to "shrinkwrap" the internal atom until it burst at C_{44}, while with an internal cesium atom it burst at C_{48} – precisely the points predicted by the known sizes of these metal atoms.

In spite of all this evidence, the fullerene hypothesis remained somewhat controversial. Although the experiments and theoretical calculations vividly demonstrated that C_{60} was a stable, closed shell molecule, all attempts at collecting it in visible amounts from the laser vaporized carbon targets and supersonic nozzles met with failure. After several years of this search, most groups assumed (as we did at Rice) that C_{60} was simply too difficult to extract from the graphitic soot produced as the dominant product of the laser vaporization.

The stage was therefore well-set for the stunning announcement[15] of the first isolation of macroscopic quantities of C_{60} in early fall of 1990. A collaboration of physicists (Donald Huffman at the University of Arizona, and Wolfgang Krätschmer at the Max Planck Institute for Nuclear Physics in Heidelberg, Germany) had long been interested in the properties of interstellar dust, and simulating this dust by generating graphitic soot in the laboratory. They discovered that one special way of generating this soot produced so much C_{60} and C_{70} that it could actually be seen by eye! All one had to do was mix a bit of the soot with clear benzene and watch the liquid turn red as the fullerenes dissolved. The soot itself was almost

Figure 4.

Schematic of cluster FT-ICR apparatus developed for the detailed study of clusters levitated in the high field of a superconducting magnet.



trivial to produce: all one had to do was condense carbon vapor produced by resistively heating a graphite rod in a 100 torr atmosphere of helium.

This amazing result would have been completely unbelievable were it not for the fact that it was almost immediately reproduced in a number of laboratories. Without question C_{60} and C_{70} were being produced in substantial yield by this simple technique. In fact, when carefully optimized, yields of these fullerenes from this Huffman-Krätschmer technique have been reported as high as 40% of all the evaporated carbon.

Within a few months we discovered that there was nothing critical in the method of resistive heating used by Huffman and Krätschmer. In fact, just a simple carbon arc run in an atmosphere of helium proved to work quite well.[16] Extensions of this nearly trivial technique have now made the C_{60}/C_{70} fullerene - rich graphitic soot available commercially in multi-gram quantities. The intrinsic costs involved appear to involve primarily the electrical power necessary to run the carbon arcs. It is therefore expected that this new form of carbon may ultimately be available at extremely low prices – perhaps as low as $5-10 per pound – once there is a sufficiently large market to warrant the investment.

The carbon arc method has been shown to produce a number of large fullerenes in substantial yield in addition to C_{60} and C_{70}. The next most abundant fullerene is found to be C_{84}, and then C_{76}, C_{78}, C_{90}, and a broad distributions of "giant" fullerenes extending out to over 200 atoms in size.[17] These individual fullerenes are readily separated and purified by standard techniques of column chromatography, though this adds substantially to their cost. In the long term, separation of these fullerenes may be done on an industrial scale using specially developed porous membranes.

Properties of the Pure Material

The archetypical fullerene, C_{60}, is a rather uninspiring brownish powder. It sublimes readily at temperatures above 350 C, and dissolves in a wide range of non-polar organic solvents. It is stable in air. Carbon-13 NMR measurements reveal that the molecule is composed of 60 equivalent carbon atoms, thereby proving the originally-proposed icosahedral soccerball structure.[18] Similar NMR studies of dissolved C_{70} proved[18,19] that it has precisely the rugby-ball structure suggested in 1985.

When sublimed, C_{60} is found to produce beautiful yellow-gold colored films of excellent cohesive quality on a wide range of substrates. Well-formed single crystals have so far best been made by slow growth from the hot vapor. X-ray diffraction studies of the crystal show that at room temperature the balls are packed in a face-centered cubic (fcc) lattice, with the nearest neighbor distance (between ball centers) of 1.003 nanometers. NMR measures of this solid form revealed that the buckyballs are spinning freely even in the crystal lattice, at speeds of over 100 million revolutions per second. When cooled, this free spinning motion switches over to a flipping

reorientation between equivalent configurations near -20° C where a phase transition occurs to a simple cubic phase.[20] This rapid flipping continues until the crystal is cooled to near liquid nitrogen temperature.

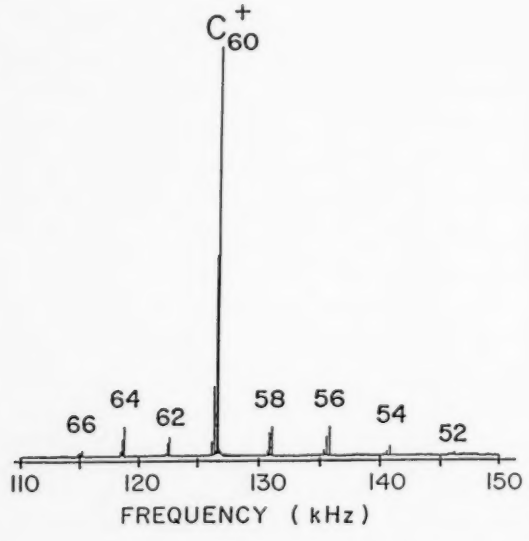
Calculations[21] have revealed that the fcc crystalline form of C_{60} should be a direct bandgap semiconductor, with a gap of roughly 1.6 eV. As such it is highly insulating at room temperature, but like all semiconductors, the conductive (and photoconductive) properties of these new materials should be highly sensitive to small amounts of dopants.

Measurements and theoretical calculations of the fundamental properties of these pure fullerenes are proceeding at a rapid pace. Basic research laboratories worldwide have contributed to something of a interdisciplinary feeding frenzy of studies on these new materials – over 200 scientific manuscripts were submitted on this topic in the first half of 1991 alone, and the rate of submissions continues to increase. In the remaining sections of this short article, only one aspect of this research will be discussed in detail – the progress so far achieved in doping these fullerenes.

But, before we leave this topic of the properties of C_{60} and the other bare fullerenes, consider again just the simplest properties: these fullerenes dissolve. They sublime. In these properties alone the fullerenes are unique among all other forms of pure carbon that mankind has ever had available. It is too early to predict with any accuracy the impact this will have on technology, but I feel confident it will be substantial. Carbon, after all, is the most versatile of all elements. Now, for the first time, it can be manipulated with great precision and cleanliness.

Figure 5.

FT-ICR mass spectrum of carbon cluster positive ions formed by laser vaporization of graphite. Note the dominant abundance of C_{60}^+.



For example, using C_{60} or C_{70}, pure carbon can now be deposited in well-defined patterns on wide varieties of surfaces without resorting to extreme temperatures. The exact chemical state of this carbon on the surface is then precisely known, and well-defined subsequent chemical or physical modification can proceed with uniform, controlled results. Collimated, intense fullerene ion beams can also be used to bombard surfaces with pure carbon. Collisions at less than 250 eV kinetic energy simply result in the fullerenes bouncing off,[22] after annealing the rough 1 nm square impact spot on the surface. Higher energies may result in fascinating picosecond timescale reactive fullerene-surface events. Alternatively, porous materials such as graphite fiber composites may be infused by exposure to fullerene vapors, and then finally baked, turning the fullerenes into amorphous graphite within the composite. Once the cost of C_{60} and C_{70} drops below something like $100 per pound. it is easy to imagine them becoming the carbon form of choice for a vast number of such applications.

Doping the Fullerenes

Easily the most exciting development to come out of fullerene research so far has been the discovery that through appropriate doping, C_{60} can be made superconducting. A group AT&T Bell Laboratories[23,24] found that C_{60} films became metallic conductors after they were exposed to potassium vapor for several hours at 250° C. The found the maximum in conductivity occurred when enough potassium had interpenetrated the buckyball film to bring the overall stoichiometry to near 3:1, i.e., to make a film of composition K_3C_{60}. Doping above this level was found to decrease the electrical conductivity, until at a composition of K_6C_{60} it became insulating again. Similar behavior has been found with the other alkali metals.[25]

This remarkable dependence of conductivity on increasing doping with alkali metals is just what would be predicted if they took up positions in the vacant spaces between the C_{60} balls in the fcc lattice. Given the high electron affinity of these buckyballs (2.65 eV) and the low ionization potentials of the alkali metals, there is little question that the metals would exist in the lattice as positive ions, having donated their valence electrons to produce negatively charged C_{60}. Alkali doped buckyball solids are therefore best thought of as conducting alkali fulleride (or alkali "buckide") salts.

As had been well established in the earliest electronic structure calculations for C_{60} and verified by photoelectron spectroscopy,[11] the lowest available molecular orbital to accept these extra electrons would be a three-fold degenerate orbital of symmetry t_{1u}. With three electrons donated from

neighboring alkali metal atoms this C_{60} orbital would be half-filled. Overlap between these t_{1u} orbitals on adjacent C_{60} balls in the fcc lattice then gives rise to a narrow conduction band for the bulk crystal. Further doping of the crystal with alkali metals would then begin to fill this band, reducing the number of effective charge carriers. At K_6C_{60} this simple model would predict that the t_{1u} conduction band would be filled, and the ~1 eV gap between this band and the next higher conduction band would cause this too-heavily doped material to behave again as an insulator.

This simple picture has now been confirmed in impressive detail. The K_3C_{60} crystal structure has been determined by x-ray diffraction analysis to be just as expected: basically it is a fcc lattice of buckyballs with potassium ions filling all of the tetrahedral and octahedral vacancies.[26] Photoelectron studies[27,28] of this material confirm that the t_{1u}-derived conduction band is half-filled, and similar results have been obtained with other alkali metals as dopants.

While these A_3C_{60} alkali buckide salts are metallic conductors, at room temperature their conductivity is quite modest – 600 ohm^{-1} cm at most, which is about 100 times lower than the conductivity of lead. But when cooled to cryogenic temperature the conductivity of these materials improves dramatically – they become superconducting at temperatures far higher than ever seen in any other molecular material.

In the case of potassium doping,[24] the K_3C_{60} material becomes superconducting at 18K. With rubidium[25] this critical temperature, T_c, has increased to near 30K. Currently the highest temperature superconducting alkali buckide material prepared[29] has been Cs_2RbC_{60}, for which the measured T_c is 33K. Researchers at Allied Signal have reported T_c as high as 45K for a thallium/rubidium doped buckide salt, suggesting the T_c of such materials may yet rise further as other dopants are tried. The fact that the supercurrent in these new high-T_c buckide superconductors is isotropic may prove to be a major advantage in the manufacturing of practical superconducting wires. Unlike the high-T_c cuprate-based ceramic materials which conduct well only along the flat CuO_2 planes in the crystalline powders, the buckide superconducting grains will not have to be aligned in any particular direction to allow strong supercurrents to flow. They are cubic crystals with isotropic supercurrents.[30]

Doping the Hard Way – on the Inside

Ever since the first announcement in 1985 that C_{60} soccerballs had been made in supersonic beams, efforts have been made to "put something inside it." The diameter of C_{60} at the positions of the carbon nuclei is 7.1 Å. Taking into account the van der Waals radius of carbon (1.77 Å), this leaves a hollow space in the inside roughly 3.5 Å in diameter – large enough to hold essentially any element in the periodic table. By judiciously choosing the central atom one ought to be able to fine-tune the electrical, chemical, and photophysical properties of the fullerene ball to obtain highly useful new properties. For example, a C_{60} ball doped with a single potassium atom inside has been calculated to be an effective n-type dopant for a semiconducting fullerene crystal.[21] Correspondingly, a C_{60} ball with an internal chlorine atom would be expected to be an effective p-type dopant. Pure crystals composed entirely of fullerenes doped internally with a metal which donates two or three electrons to the carbon cage may be even better superconductors that the externally doped alkali fullerides.

Such internally-doped fullerenes have been given the name "endohedral complexes."[31] In recent work where some of these have been synthesized for the first time, a new symbolism has been proposed.[32] For example an endohedral C_{60} - barium complex will (in the new symbolism) be written as ($Ba@C_{60}$). Here the normal symbols for atoms which are involved in the fullerene structure are gathered within a set of parentheses containing the symbol "@". Atoms which are inside the hollow fullerene cage are listed first, to the left of the @ symbol, while those which are used to construct the cage itself are listed to the right. Although fullerenes thus far have only been isolated with carbon atom cages, it should be possible to exchange some of thee carbon atoms with atoms of boron or nitrogen. As will be discussed briefly below, there is already some evidence for the efficient production of the boron-substituted endohedral complex fullerenes ($K@C_{59}B$) and ($K@C_{58}B_2$).

The first evidence of successful inside doping was obtained within a week of the 1985 experiments on C_{60}. A porous graphite disc was impregnated with lanthanum trichloride and mounted in the laser vaporization supersonic cluster beam source.[33] In addition to C_{60}, C_{70}, and a broad distribution of other fullerenes there were also even-numbered carbon clusters present with a single lanthanum atom attached. The fact that only one La atom appeared to be bound to the clusters and that it remained attached when probed at extremely high laser fluences was taken as evidence that the La atom had actually been trapped inside to make a distribution of ($La@C_n$) clusters.

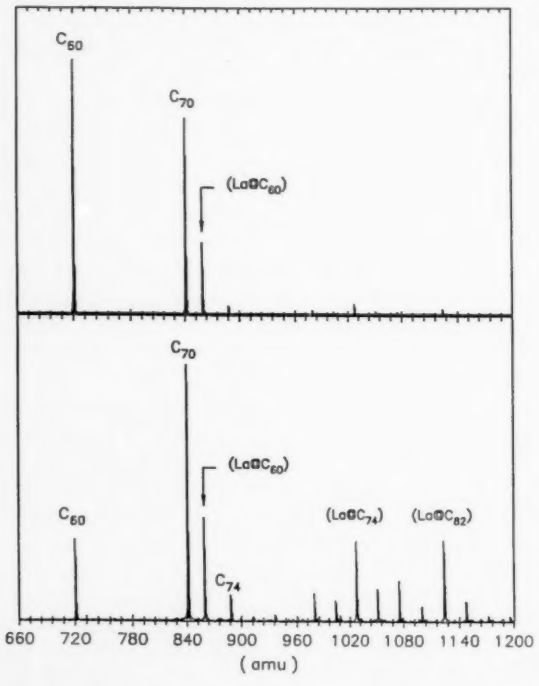
Several years later this evidence was supported quite dramatically by experiments in a powerful new apparatus which we had developed in our laboratory for the general study of cluster structure and chemistry. Here a supersonic cluster beam produced by laser vaporization was directed into the bore of a superconducting magnet. Here electrodes were provided to slow the clusters down and trap them as positive ions, levitating them in the magnetic field at high vacuum. A schematic of the most recent version of this apparatus[4] is shown in Figure 4. This apparatus is particularly powerful since the cyclotron motion of the cluster ions in the uniform magnetic field can be used to detect their presence and measure their

mass with extremely high mass resolution. For example, Figure 5 shows a well resolved mass spectrum of carbon clusters produced by laser vaporization of graphite. The effective mass resolution of such a Fourier Transform Ion Cyclotron Resonance (FT-ICR) technique is typically 50,000 to 1 or higher.

In the case of metal-fullerene complex clusters there are two key advantages of this apparatus. First, the trapped cluster ions can be exposed to any of a wide variety of reactive gases to see if the metal atom is exposed. Metals like lanthanum are known to be extremely reactive with air and water. In fact, when lanthanum metal is deposited on the surface of graphite particles it is pyrophoric, bursting into flame as it burns in air to form first the very stable LaO molecule, and then the La_2O_3 crystalline oxide. Yet, the lanthanum-carbon cluster ions produced by laser vaporization of $LaCl_3$/graphite composite target disks were found in the new FT-ICR apparatus to be completely inert toward a wide variety of reagent gases, including O_2, NO, water, and ammonia, suggesting the lanthanum atom actually was trapped inside clusters of the form $(La@C_n)^+$.

Figure 6.

FT-ICR mass spectrum of air-stable sublimed fullerene film showing presence of cage-trapped lanthanum species ($La@C_n$). The top panel was obtained under conditions optimized for detection of clusters in the range around C_{60}, the bottom panel is optimized for clusters around ($La@C_{74}$).



The second key advantage of the FT-ICR apparatus in studying metal-fullerene complexes was that they could be exposed to intense lasers, and their photofragments examined at high mass resolution. As mentioned earlier, the fullerenes as a class have been shown to be incredibly photo resistant.[13] When they do finally fragment, they do so by shrinking to form the next smaller fullerene. We were able to show that the lanthanum-carbon cluster ions behaved in this same way. The $(La@C_{60})^+$ cluster ion, for example, was found to fragment by successive C_2 losses, just as C_{60}^+. But unlike C_{60}^+ where this shrinking process continues down to C_{32}^+ before the fullerene cage finally bursts, the $(La@C_n)^+$ granddaughters of the fragmentation of $(La@C_{60})^+$ could not be shrunk below $(La@C_{36})^+$. This is about what one would expect based on the ionic radius of an internal lanthanum ion in the +3 charge state. Fullerene cages smaller than C_{36} are just too small to wrap around a La^{+3} ion.

Similar experiments verified that $(K@C_n)^+$ and $(Cs@C_n)^+$ cluster ions could be made and levitated in the cluster FT-ICR apparatus. All such clusters were found to be inert toward oxygen and water, and all were found to fragment upon intense laser photolysis simply by the successive loss of C_2. In the case of potassium the smallest stable fullerene seen in the laser "shrinkwrapping" experiment[14] was $(K@C_{44})^+$, while for cesium it was found to be $(Cs@C_{48})^+$ – both in perfect accord with predictions based on the known ionic radius for these alkali metals in the +1 charge state.

By 1988, therefore, it was clear that fullerenes with metals trapped inside could be made by condensation of laser-vaporized metal/graphite targets in at least microscopic amounts. However, until the Huffman-Krätschmer technique was announced in Sept. 1990 there was no known technique for the production of visible, macroscopic amounts of any fullerene. But once their resistively heated carbon rod technique and the subsequent carbon arc methods were successfully reproduced in labs throughout the world for the production of C_{60} and other small empty fullerenes, the interest of many groups turned to efforts at producing gram quantities of $(M@C_n)$ caged-metal clusters as well.

For many months none of these groups met with any success. The metallofullerenes may have been produced, but no one could extract them from the resulting carbon soots. Just recently, however, this situation has changed. Chai et al.[32] have reported the successful extraction of a small amount of one particular lanthanum fullerene, $(La@C_{82})$, from a standard carbon arc fullerene synthesis apparatus. They used graphite rods which had been bored-out and packed with a 10% mixture of La_2O_3 in graphite powder. But most significantly they reported much better results from a modification16 of the laser vaporization technique originally used on 1985. Here a graphite/La_2O_3 composite rod is mounted in a quartz tube furnace

operating at 1200° C. Laser vaporization of this composite rod as it rotates in the oven to maintain a smooth surface was found to produce both empty ($@C_n$) fullerenes and ($La@C_n$) metallofullerenes in abundance[32,34]. These mixed fullerenes could be sublimed onto a cooled copper disk and transported through air in the form of a shiny black nearly mirror-quality film. Gentle laser desorption of these sublimed films followed by ionization and trapping in the FT-ICR apparatus showed mass spectra similar to Figure 6. These films clearly contain ($La@C_{60}$) and a range of larger ($La@C_n$) species imbedded in a protective matrix of C_{60}/C_{70}.

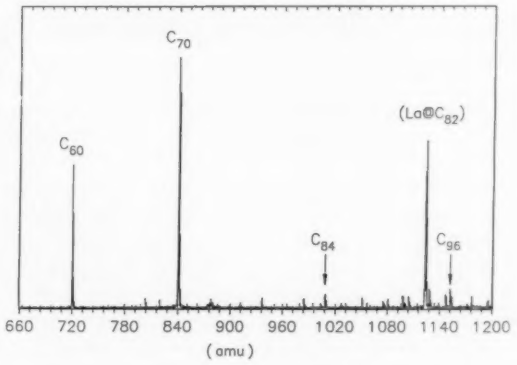
When these films were dissolved in hot toluene, or the original laser-vaporized carbon/lanthanum soot produced in the quartz tube furnace was extracted with refluxing toluene, the resultant solution when carefully filtered showed that only one lanthanum fullerene species could be extracted: ($La@C_{82}$). This is evident in the mass spectral analysis of Figure 7.

The unique extractability of this species in hot toluene solutions is thought to be a consequence of the quantum mechanics of these metallofullerenes. Chang, Ermler, and Pitzer[35] have calculated that an internal lanthanum atom will effectively donate both of its valence 6s electrons to the delocalized "π" orbitals of the fullerene cage. In the case of ($La@C_{60}$) the result is that the molecule will be electronically open shell with two electrons in the t_{1u} LUMO of the C_{60} cage. The next most stable fullerenes, C_{70} and C_{82}, would be expected also to result in open-shell electronic structures when lanthanum atom is trapped inside. Such a species may be fairly reactive when exposed to air or moisture, or they may form stable but not readily soluble charge transfer complexes with C_{60}. But C_{82} with an additional two electrons from an internal lanthanum atom will have an 84 electron "π" shell count, and is likely a closed shell species with a substantial HOMO-LUMO gap. Detailed calculations on possible structures for ($La@C_{82}$) are currently in progress to test this hypothesis.

The long term significance of ($La@C_{82}$) may be not so much in the usefulness of its properties, but simply that it appears to be the first extractable metallofullerene. Work is underway now to chromatographically purify it, and to probe the nature of its internal La atom by such techniques as X-ray photoelectron spectroscopy (XPS). Once crystals are obtained the x-ray structure should follow rapidly. But stimulated by this success, much more work can be expected follow on other metallofullerenes. The fact that most of these will be open-shell species simply means that they will have to be handled by other techniques. The fact that C_{60} films seem to provide a safe means of transporting the other ($La@C_n$) species may be very useful. Once in a controlled, inert atmosphere they can be dissolved in appropriate solvents and rendered stable either by derivatization, or by the formation of stable metallofulleride salts. Now that at least small quantities of these new cage-trapped materials are available, we can begin the process of learning their chemical and physical properties. This information, in turn, will help in devising large-scale production strategies.

Figure 7.

FT-ICR mass spectrum of hot toluene extract of lanthanum fullerene material made by laser vaporizing a graphite/La_2O_3 composite rod in an oven at 1200C. Note that ($La@C_{82}$) is the only lanthanofullerene to be extracted with good yield.



Doping Another Hard Way – in the Cage

An alterative kind of doping would be to replace at least some of the carbon atoms in the fullerene cage structure itself with some other atom. Boron or nitrogen atoms, for example, would be nearly perfect substitutions for carbon in such a 3-connected graphitic network both from considerations of size and chemical valence. In fact, evidence for the efficient production of boron-doped fullerenes has already been obtained in laser vaporization experiments using boron/graphite composites[36]. As expected, the boron atom sites on the surface of the fullerene are electron deficient and act as Lewis acids. Experiments in the cluster FT-ICR apparatus show that they can be readily titrated with ammonia. Fullerenes in the 60-100 atom size range have been made by these laser vaporization techniques with up to 6 boron atoms substituting for carbons in the cage. Laser photolysis shows that the first couple B-substitutions survive the C_2 evaporative shrinking process all the way down to the 32-atom normal bursting limit, many of the final 32-atom fullerenes having the composition ($@C_{31}B$) and ($@C_{30}B_2$). Considering the extremely high effective temperatures attained during this shrinking process, this is an impressive indication of the stability of boron-doped fullerenes.

As yet no sublimable or solvent extractable boron "dopyballs" have yet been produced, although there is some evidence[32] that the presence of compensating dopants such as

potassium amy result in at least small amounts of stable, sublimable doubly-doped fullerenes such as ($K@C_{59}B$). The problem is most likely one of preventing polymerization of the boron-doped fullerenes with each other.

Other Strategies for Intrinsically-Doped Fullerene Production

The above methods produce doped fullerenes at the moment of the fullerene synthesis itself, presumably growing the fullerene cage around a metal atom and/or attaching a boron atom to the edge of the cage while it is still in the hot condensing carbon vapor. In the case of metals this may work well for elements on the left hand side of the periodic table, but it is unlikely to be readily extended to the right hand side. The currently favored theory for the efficient formation of fullerenes in the size range around C_{60} is that open graphitic sheets curl as they anneal at high temperatures through the incorporation and appropriate spacing of pentagons in their structure[1,16]. This is a high temperature process – proceeding efficiently only above 1000 C. In order for some atom other than carbon to be efficiently retained in this curling hot structure it must be fairly strongly bound. It is expected that the fairly electropositive metals successfully trapped thus far (Na, K, Rb, Cs, Ca, Sr, Ba, Y, La, and U) are able to ride out this annealing, curving process by forming an effective charge-transfer complex with the graphitic sheet. Other metals with higher ionization potentials may not "stick" sufficiently tightly by this mechanism to ride out the closure process. In fact our repeated failures to make ($Fe@C_n$) and ($Cu@C_{82}$) clusters by laser-vaporization techniques may be due to this problem. Given their relatively high ionization potentials, they just don't stick on to the curling graphitic sheets long enough. Even with major success in producing stable endohedrally-doped fullerenes like ($La@C_{82}$), it seems likely that entirely different strategies will be necessary to extend study and use of such complexes to the rest of the periodic table.

One alternative method that has recently received some favorable support is direct ion implantation. Rather than doping the fullerenes as they are formed initially, in might be possible to put something inside later simply by blasting it in. Indeed, with small atoms such as helium, lithium, and hydrogen, this may be the method of choice. In a beautiful series of experiments in a number of labs very recently[37,38], the first successful collisional implantations have been carried out with fullerene ion beams. Fullerenes like C_{60}^+ and C_{70}^+ accelerated up to kilovolt energy have been passed through low pressure gas cells filled with gases such as helium. When the center of mass collision energy exceeds roughly 15 eV, it is found that the cluster ions passing out the exit of the gas cell have picked up a helium atom. Ross and Callahan were able to prove that the species produced were $(He@C_n)^+$ ions by passing them through another collision cell with Xe gas and showing that the helium atom could not be removed – C_2 evaporative "shrinkwrapping" was the only process observed. When too much translational energy is used in the collision fragmentation becomes extreme, producing $(He@C_n)^+$ where n is considerably less than 60. But in the range of 15-40 eV a significant fraction of the original C_{60} ions survive the He atom implantation. Any carbon-carbon bonds broken on initial entry of the helium atom into the center of the cage are subsequently healed before the atom can escape, and the overall energy deposition into the structure is insufficient to produce C_2 evaporation at a significant rate.

Such experiments raise the interesting possibility that doped fullerenes might be produced effectively by an extension of the ion-implantation techniques currently used to dope semiconductor films. Imagine, for example, a device which deposits C_{60} on metal substrate by sublimation of a pure C_{60} sample in an oven while simultaneously bombarding this film with lithium ions at energies in the 10-100 eV range. The Li^+ ion is considerably smaller than He, so it is reasonable to expect that a this lithium ion implantation device might produce a substantial number of ($Li@C_{60}$) fullerenes which, because they have adjacent pentagons, will be rather unstable; and many of the lithium atoms will end up outside the fullerene cages. But a subsequent work up of this film by sublimation, or dissolution in appropriate solvents may permit the ($Li@C_{60}$) material to be isolated in useable amounts.

In view of the likeliness of a small amount of fragmentation accompanying this direct ion implantation process, it may be best to start with C_{70} as the initial fullerene target. This initially impregnated ($Li@C_{70}$) "egg" would then get rid of its excess energy, in part, by fragmenting (shrinkwrapping) down to ($Li@C_{60}$). although pure C_{70} is currently a very expensive starting material, it is made in considerable abundance in carbon arcs[15,16] and sooting flames[39], and should ultimately be a rather inexpensive commodity.

Fullerene Chemistry - A Carbon-Based Nanotechnology

In addition to such physical, brute-force, methods of producing metal-filled fullerenes, there will almost certainly be effective chemical routes developed to achieve the same ends. Starting with pure C_{60}, C_{70}, or larger fullerenes, it seems reasonable to hope that future fullerene chemists will be able to open up the cage in a controlled manner, cut it down by a desired amount, and reassemble these cage-parts again, trapping desired atoms or molecules in the inside.

As a side benefit, this fullerene chemistry of the future may permit the synthesis of a wide range of interconnected

fullerene cage structures, or even hollow graphitic cylinders which are almost exactly 1 nanometer in diameter[40]. It is made up of two hemispherical end caps composed of a central pentagon connected along bonds between hexagons to five other pentagons. In C_{60} these two hemispherical bowls are connected directly to each other after a rotation by an angle of $\pi/5$ so that they mesh perfectly with one another. In C_{70} they are connected together (without rotation) by meshing with a central belt of five hexagon wide. But, in principle, there is no reason it could not be two hexagons wide to make a cylindrical C_{90}, or three to make C_{110},..., or hundreds of thousands of hexagons wide, producing such a long cylinder that it would better be termed a hollow graphite tube or fiber. It would be the most perfect, defect-free graphite fiber ever produced. Other end caps are available for such tubes, producing fibers of larger internal diameter and different over-all symmetry. Tubes made up of multiple coaxial layers are, of course, also conceivable.

Some possible evidence for the formation of such hollow carbon cylinders has already been published even before the advent of a rational constructive fullerene chemistry. Wang and Buseck[41] has published high resolution transmission electron micrographs of C_{60} films where the 400 eV electron beam has apparently generated hollow cylindrical structures 1 nm diameter and 2 or 3 nm long. It appears possible that inelastic interactions of the electron beam with some of the C_{60} cages has caused a coalescence reaction to produce 120 atom cylindrical dimers. Such C_{60}-C_{60} coalescence reactions have been observed in laser desorption experiments from pure fullerene films[42,43]. They have also been invoked in the case of ($La@C_n$) clusters to explain the generation of large fullerene-caged La_x clusters[32] such as ($La_3@C_{110}$). One would, of course prefer to have a more controlled, low energy route developed for generation of such structures.

Some day fullerene chemists may learn how to manipulate not only fullerenes, but fullerene fragments. In addition to fullerenes opened at one end, producing something of a tiny chemical purse into which atoms, ions and small molecules can diffuse, it is possible that fullerenes opened at both ends would be highly useful. These short sections for graphite cylinders may serve as effective building blocks of a wide range of nanometer-sized architectures. Interconnected with intervening fullerene cages, doped with desired internal atoms, and derivatized on the outside with desired side groups, the technological implications of these new carbon-based nanostructures may be dazzling.

Biography

Professor Smalley is featured as "Profiles in Science" on page 15 of this issue.

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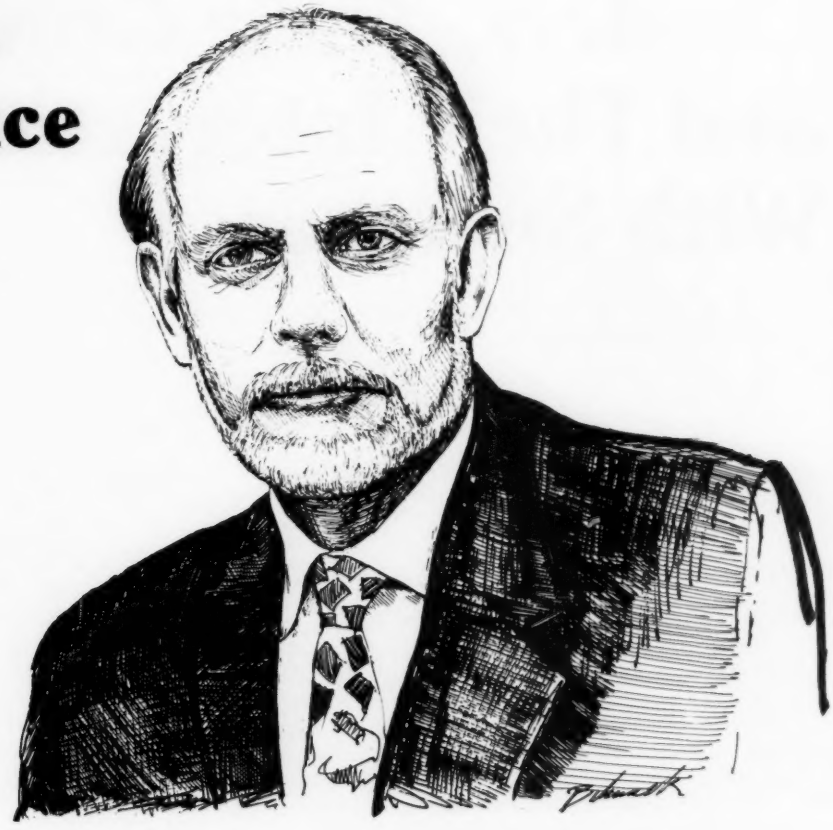
Profiles in Science



Professor Richard Smalley

Professor Smalley received his B.S. degree in 1965 from the University of Michigan and Ph.D. from Princeton in 1973, with an intervening four year period in industry as a research chemist with Shell. During an unusually productive postdoctoral period with Lennard Wharton and Donald Levy at the University of Chicago, he pioneered what has now become one of the most powerful techniques in chemical physics: supersonic beam laser spectroscopy. Since coming to Rice University in 1976 he has risen rapidly through the academic ranks, being named to the Gene and Norman Hackerman Chair in Chemistry in 1982. He was one of the founders of the Rice Quantum Institute in 1979, and has served as the chairman of this interdisciplinary Institute since 1986. Since January 1990 he has also been a Professor in the Department of Physics at Rice. In April of 1990 he was elected to the National Academy of Sciences. He is the recipient of the 1991 Irving Langmuir Prize in chemical physics, awarded by the American Physical Society. His research at Rice has made pioneering advances in the development of new experimental techniques (super-cold pulsed beams: ultrasensitive laser detection techniques; laser-driven source of free radical, triplets, metals, and metal cluster) and has applied these techniques to broad range of vital questions in chemical physics. He is widely known for the discovery and characterization of C_{60} (buckminsterfullerene), a soccerball-shaped molecule which, together with other fullerenes such as C_{70}, now constitutes the third elemental form of carbon (after graphite and diamond). His current research is directed toward the development of a new approach to surface science and catalysis. In this new "molecular surface science", small clusters of metal (or semiconductors) consisting of only 10 to 100 atoms are used as tiny molecular models of the bulk surface – models that are large enough to display real surface chemistry and physics, but small enough for theorists to handle at a detailed and predictive level.

Clusters, Their Growth, and Their Interaction With Surfaces

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Introduction

Clusters play an important role in science and technology, as is evident from their prevalence in catalysis, dispersed magnetic media, abrasives, photographic emulsions, and heterogeneous nucleation. This paper explores their role in processes related to thin film growth on surfaces. In turn, overlayer growth, thin films, and interfaces are vital in electronic devices, the incorporation of materials such as the high-temperature superconductors or diamonds in multicomponent systems, the development of supported catalysts, the synthesis of composites, and the creation of advanced materials.

Clusters represent the middle ground between atoms and nanocrystals. Their properties reflect their geometric structure, their size, and whether they are supported or free standing. During the formation of an interface, the clusters that appear represent the seed of the overlayer. For nonreactive overlayers, these seeds are elemental in character as, for example, for Ag on GaAs. For reactive systems, they are composed of two or more elements, as for Ti deposition onto GaAs. One of the most important points of this paper is that the interactions of a cluster on a surface will change as the number of atoms in the cluster increases and these effects dictate the chemical and structural stability of the contact. We will stress this point by considering Al cluster formation on GaAs(110) where the small clusters are weakly interacting but they induce intermixing when they grow.

This review will focus on two different forms of clusters, their interaction with surfaces, and their roles in overlayer formation. First, we will discuss clusters that are produced spontaneously on a semiconductor surface, or any surface for that matter, when adatoms are deposited onto that surface. We will then examine clusters that are formed remotely but are then brought into contact with the surface. We will show that the latter process yields a different "state" because the process avoids the "chemistry" associated with atom-by-atom deposition and assembly on a surface. The experimental emphasis will be on the techniques of photoemission and scanning tunneling microscopy, because they make it possible to explore bonding sites, clustering, reaction pathways, and overlayer formation.

Atom Deposition and Spontaneous Clustering; Al/GaAs(110)

Most methods of solid-solid interface formation involve the condensation of single atoms of the overlayer material onto a prepared substrate.[1] These atoms are generally produced by evaporation from hot sources, by sputtering, or by gas-phase reactions. Their kinetic energies are determined by the source itself, and the condensation process releases additional energy as bonds are formed at the new solid surface. When the number of atoms deposited is very small, they are probably isolated from one another even though they may be quite mobile. As the number of adatoms increases, however, overlayer growth structures are produced. These structures are dictated by adatom interactions with the substrate and with one another as well as the kinetics associated with assembly.

As an example of overlayer growth dominated by spontaneous cluster formation, we consider Al deposition onto GaAs(110) at 300 K.[2] The results discussed below were ob-

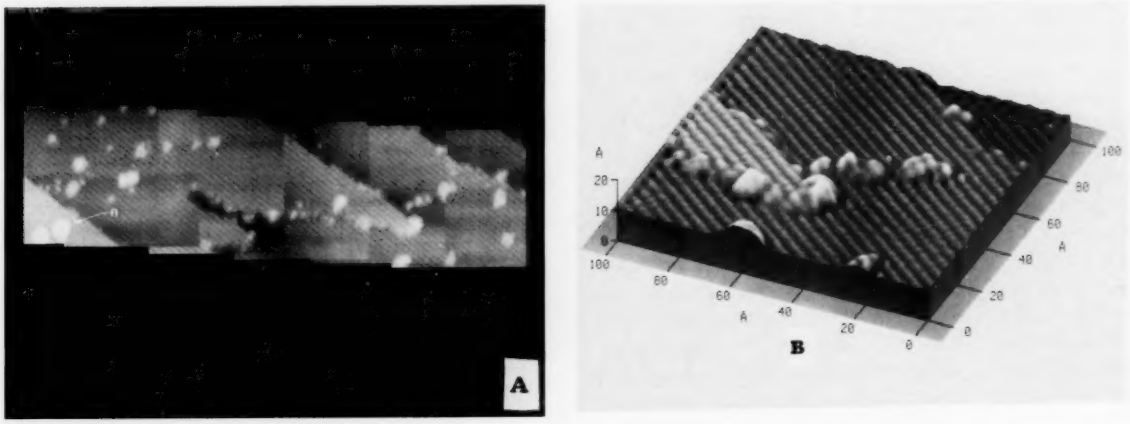
tained in scanning tunneling microscopy experiments in an ultrahigh vacuum chamber at a pressure of ~$6x10^{11}$ Torr. GaAs(110) surfaces were prepared by cleaving. We will discuss results for stepped and unstepped surfaces to examine the role of the step edge in clustering. Tungsten tips were prepared by electrochemical etching followed by electron bombardment heating. Aluminum was evaporated from resistively-heated baskets at pressures lower than $4x10^{-10}$ Torr. For Al, the deposition of 1.47 Å will produce the equivalent of one monolayer (ML) on the GaAs(110) surface, assuming one adatom for each Ga and As surface atom (planar density $8.85x10^{14}$ atoms/cm^2). The STM images were taken in the constant current mode with currents between 0.1 and 1 nA. For these images, the tip was biased positive relative to the sample with voltages ranging from 2 to 4 volts.

The cleaved GaAs(110) surface has been well characterized with STM images obtained using positive and negative tip biases to emphasize As and Ga sites, respectively.[3] Figure 1(a) shows a mosaic of images for 0.015 ML of Al condensed onto a stepped surface. The rows of As atoms are clearly visible along the [1T0] direction of the large terraces. Steps that are approximately parallel run from upper left to lower right along [1T0]. The large terrace on the left is terminated by an irregular step in the center of the figure. The bright features at the irregular step edge are small Al clusters. Significantly, the results of Fig. 1 show that the more regular [1T0] steps do not serve as preferred nucleation sites.

The deposition of 0.015 ML of Al produced clusters (that contain as many as ~40 atoms) on the terraces. The volume of the cluster labelled A at the left of Fig. 1(a) was estimated to be 535 $Å^3$, corresponding to ~32 atoms, as determined by integrating the height contours of the STM image.[4,5] A 3D-rendered image from the mosaic is shown in Fig. 1(b) to provide a perspective of cluster heights relative to contact area. Cluster formation occurred even for the lowest coverage studied (0.015 ML), and chemisorption of individual atoms could not be identified. This is not surprising because adatoms having sufficient thermal energy can surmount the potential barrier, E_b, for surface diffusion. Such thermally activated hopping is largely based on estimates using typical vibrational frequencies and the barrier for diffusion.[6] The STM results provide particularly important insight into the bonding of the clusters

Figure 1.

STM images and a cross section for 0.015 ML Al deposition on a stepped GaAs(110) interface at 300 K. (a) 475x175 $Å^2$ area acquired with a tip bias of 3.8 V and 0.1 nA showing large terraces decorated with Al clusters, [110] steps (labeled S) with almost no Al, and clusters at the irregular terminals of the large terrace (labeled I). (b) a 125x125 $Å^2$ 3-D rendered image displayed to enhance the curvature.



to the surface because the tip occasionally displaced a cluster. Figure 2(a) shows an image for a highly stepped surface onto which 0.07 ML of Al had been deposited. The arrow indicates a cluster with a diameter of 25 Å and a height of ~5 Å consisting of ~40 atoms situated on a step. This cluster was displaced upon subsequent scanning, as shown by Fig. 2(b). The other surface features appeared unchanged, and the atomic resolution of the tip was maintained. Examination of Fig. 2(b) shows that the substrate exposed by cluster displacement was not different from other exposed sites on the surface. We conclude that clusters with ~40 atoms are weakly interacting with the substrate and do not induce surface disruption. As will be discussed below for higher coverages, however, footprints were left behind when larger clusters were displaced.

Figure 3(a) shows a 1400x1400 $Å^2$ image obtained after 0.3 ML deposition of Al on a surface with [1T0] monatomic steps defining large terraces. The pointed structure that originates at the upper left and terminates near the lower right is a single layer above the terrace beneath it. In Fig. 3(a), the Al clusters are typically 35-60 Å in diameter and 8-15 Å high. The higher resolution image of Fig. 3(b) shows a typical cluster labelled A with a volume of ~4760 $Å^3$ and the contact area of ~1520 $Å^2$, corresponding to ~290 atoms. In addition, there are small protrusions along the [1T0] steps that have been observed on clean cleaved stepped surfaces; they are not due to Al accumulation at the steps.

The STM image of Fig. 3(c) shows a 400x400 $Å^2$ step-free area. Comparison to Fig. 3(a) indicates that the clusters are randomly distributed on both the stepped and unstepped surfaces and there is no preferrential bonding at [1T0] steps. For both surfaces, the cluster density was 1-3x10^{12} clusters/cm^2 for 0.3 ML deposition and the cluster diameters ranged from 35 to 60 Å.

Comparison of Figs. 3(a) and 3(b) reveals that the 50-Å diameter cluster marked by an arrow in Fig. 3(a) was removed upon subsequent scanning. The footprint left by the cluster is ~25 Å in diameter and 5 Å in height, as shown by cross-sectional analysis of the region before and after removal.[2] We associate the complex footprint with Al-GaAs intermixing beneath the cluster. This agrees with medium-energy ion scattering[7] results that suggest chemical interaction beneath the clusters. In addition, photoemission results for Al depositions as low as 0.14 ML have demonstrated that Ga atoms released from the substrate mix in the Al clusters.[8] Although the dynamics of the process are not known, it appears that cluster size is the critical parameter in determining whether they are stable on GaAs(110). This can be understood by recognizing that the Al/GaAs system is thermodynamically unstable because the heat of formation of AlAs is 10 kcal/mol higher than for GaAs, and Al-Ga exchange has been reported. Such reaction is not found for single Al atoms weakly interacting with the surface or for small clusters. As the cluster grows, however, its relative stability on the surface changes so that at some point intermixing is favored. A critical coverage threshold has also been used to explain photoemission results for Ce growth on Si(111),[9] rare earth growth on GaAs,[10] and Cr growth on GaAs,[11] with differences related to the specifics of the adatom order and substrate stability. Such effects are not observed for Ag/GaAs where reaction is never favored.[12] At the other extreme, it is not observed for Ti/GaAs because reaction is so energetically favored that it occurs for single Ti atoms on contact.[13]

Figure 2.

STM images for 0.07 ML of Al on a stepped GaAs(110) surface. Both images are 100x100 $Å^2$ and were obtained with a tip bias of 2.5 V and a tunneling current of 0.6 nA. The cluster bonded to the step in (a) was displaced after repeated scanning and the now-exposed area in (b) shows no modification of the surface beneath the small cluster.

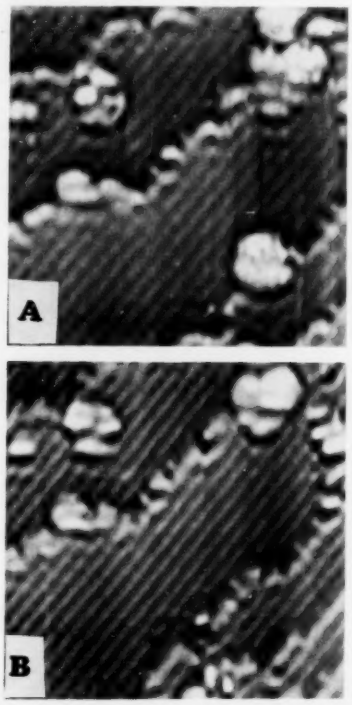
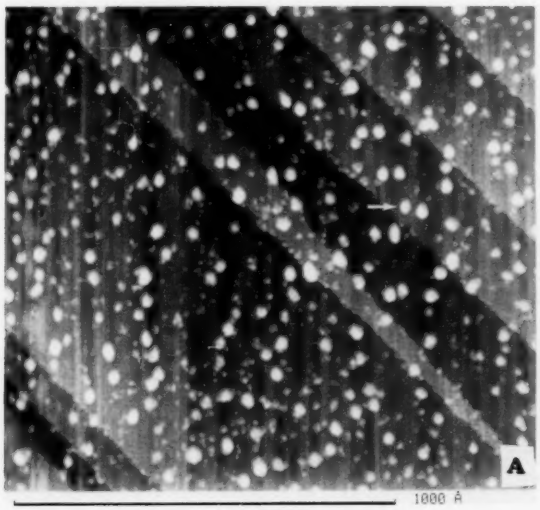
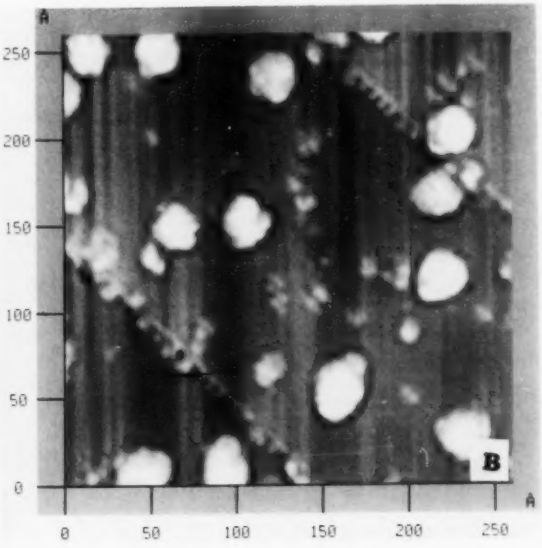


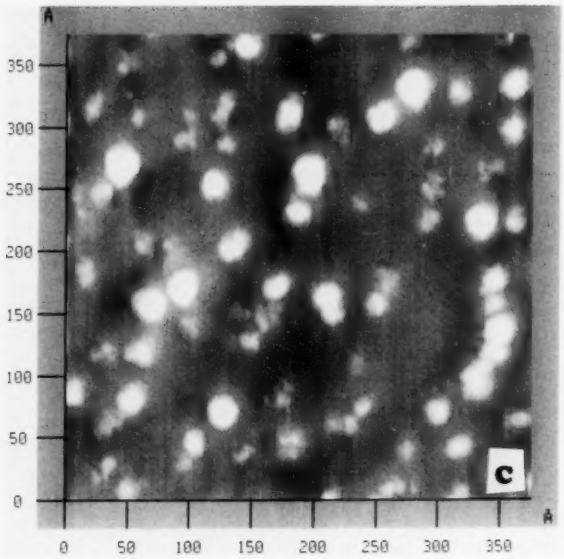
Figure 4 shows an STM image for 30 Å of Al deposited on a stepped GaAs(110) surface. The image and cross sections of various features of the surface demonstrate that the surface roughness does not change appreciably with growth. Indeed, the grain size of the polycrystalline film observed after 100 Å deposition resembled those at 10 and 30 Å, and there was no tendency to form an atomically smooth surface (surface rms roughness 2.5-3.5 Å). The maximum peak-to-valley distance was ~25 Å for the 30 Å coverage and the aspect ratio of a

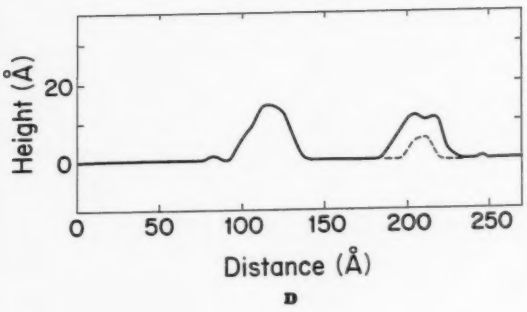
Figure 3.

STM images showing a GaAs(110) surface with [$\bar{1}10$] steps onto which 0.3 ML of Al had been deposited. The clusters appear randomly distributed with no preferential bonding to the step edges. (a) shows a 1400x1400 Å^2 image acquired with a tip bias of 3 V and 0.1 nA. (b) shows a higher resolution 260x260 Å^2 image of the boxed region of Fig. 3(a). The cluster marked by an arrow in Fig. 3(a) is missing in (b). The footprint left by the cluster is marked with an arrow in the figure. (c) shows a 400x400 Å^2 image of clusters on a step free area. (d) shows a cross section of the cluster identified in (a) and (b) before (solid line) and after removal (dashed line).









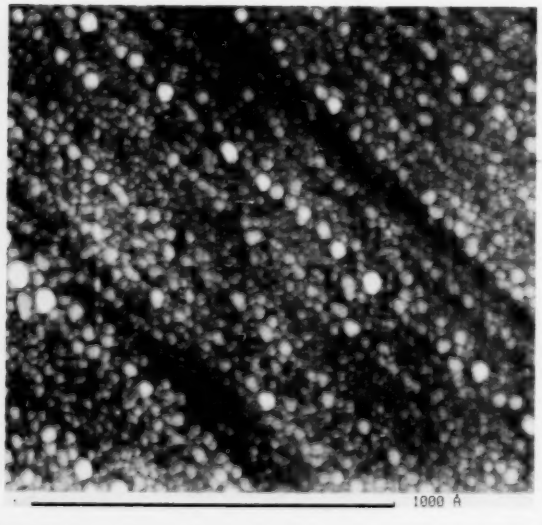
typical grain was ~0.25. We speculate that the fine grain structure results from the small ratio of the substrate temperature to the melting temperature of Al during deposition. Increasing the substrate temperature will probably result in larger grains because of the increased Al surface diffusion.

There is no evidence of the formation of Al clusters that evolve into distinct crystallites with faceted surface as for Ag/GaAs(110) growth at 300 K.[12] Instead, the fine grained morphology resembles that for the weakly reactive Fe/GaAs(110) interface where Dragoset et al.[5] reported features with 40-50 Å diameters and an rms roughness of ~3 Å after 10 Å deposition of Fe. The evolution of the reactive Cr/GaAs(110) interface[11] showed similar asperities for all coverages and a surface rms roughness of ~2.3 Å after 5 ML deposition. In each case, growth is influenced by kinetic constraints.

Thus far, we have considered interfaces for which clustering occurred spontaneously following atom deposition and then strongly influenced overlayer evolution. Such clustering at the interface is the norm rather than the exception, but it is only now possible to correlate structure (with STM) and chemical bonding (with photoemission).

Figure 4.

STM image of 30 Å of Al on GaAs(110). This 1400x1400 Å^2 image was obtained with a tip bias of 3.1 V and tunneling current of 0.15 nA. It shows surface grains with sizes up to 60 Å and an overall rms surface roughness of 2.5-3.5 Å. The alignment probably reflects the existence of multiple height steps on the cleaved surface. Growth to 100 Å of Al at 300 K resulted in equivalent surface roughness and appearance.



Cluster Assembly and Overlayer Formation

Varying the growth parameters can provide considerable insight when examining the properties of an overlayer/substrate system. Ultimately, it is desirable to determine how the growth conditions can be manipulated to control the final properties. For atom deposition, growth is initiated when individual atoms contact the substrate surface. As discussed above, substrate disruption accompanied by intermixing of substrate and overlayer atoms generally occurs for metal/semiconductor interfaces, even at low temperature. As a result, the boundary is neither abrupt nor defect-free, and its properties reflect that intermixing.

We recently developed a process that yields abrupt, defect-free interfaces by exploiting the properties of clusters. These interfaces thereby represent a final state that cannot be reached by conventional atom deposition and they have potential use in a wide variety of areas. To avoid reaction, it was necessary to minimize or eliminate direct atom-substrate interactions. We speculated that this could be done by preforming clusters composed of hundreds or thousands of atoms so that their deposition onto the surface would resemble the contacting of two large objects. Hence, constraints related to solid-solid interactions could be exploited. The trick, of course, was to first create large, clean clusters and then to condense them onto a pristine surface. The process we developed was simple, and it is flexible enough to allow investigations into new forms of composites, with applications in electronics, magnetism, catalysis, and adhesion.

Figure 5 depicts our approach to cluster assembly. First, multilayers of Xe are condensed by sample exposure to partial pressures of 10^{-6} Torr at temperatures of ~50 K. Rare gas solids are ideal buffer layers because they do not modify the substrate, and they can be easily desorbed. Following restoration of 10^{-11} Torr conditions, the rare gas layer is exposed to a flux of atoms evaporated from a thermal source in a conventional manner. On the Xe layer, the adatoms have sufficient mobility to form clusters, even at 50 K.[14] While such cluster formation is still an exothermic process, the energy is dissipated by the rare gas solid and it does not contribute to substrate disruption. Initial deposition yields Ag clusters that are covered with a Xe skin, as shown in Fig. 5 for Ag/Xe, as well as a small number of imbedded Ag atoms. The experimental results have shown that, with time, these clusters sink into the Xe layer.[15] Such motion requires that the Xe layer be pliable enough that a cluster can travel through it when there is a net force between it and the substrate. That force, schematically represented by the springs in Fig. 5, is the van der Waals force.[15,16] The van der Waals attraction is separable into a material-dependent factor, expressed by the Hamaker constants, and a geometric factor. For the attraction between a sphere of radius R and a plane, the force varies as x^{-2} for distances that are small

compared to R. For larger values of x, the force varies as x^{-4}. The compressibility of solid Xe is ~100 times greater than is typical for metals, indicating that the Xe film can undergo substantial deformation under load. This deposition process can be accelerated by subliming the Xe layer. Since the clusters are held by the van der Waals attraction, they are gently deposited onto the substrate.

Cluster assembly has now been used to form novel overlayers on semiconductors[16] and on the high-temperature superconductors (HTS),[17] and variations on the idea have made it possible to assemble clusters coated with CO.[18] Each cluster is composed of hundreds of atoms, and the resulting interface is characterized by markedly less reaction compared to overlayers that are grown atom-by-atom. For most metallic overlayers grown on semiconductor substrates, Fermi level pinning positions have been observed.[14] For overlayers on HTS materials, cluster assembly at low temperature produces a contact for which the substrate has been modified only minimally by the overlayer it does not produce the highly disrupted, oxygen-depleted insulating surface region known to form upon atom deposition.[17,19]

Transmission electron microscopy results for cluster assembly

An idea of the morphology obtained by cluster assembly can be gained from the TEM images of Fig. 6 for Cu clusters deposited onto silica layers supported by conducting Au grids.[17] The upper panel shows a TEM image for 2 Å Cu(cluster)/silica where irregularly shaped features cover ~25% of the surface. A few clusters appear elongated, probably because two or more joined during Xe desorption. If the individual clusters are taken to be circular, then the cluster size distribution peaks at ~45 Å diameter and most have diameters between 35 and 55 Å. A 45-Å diameter cluster would have an average thickness of 8 Å and would contain 750-1000 atoms, based on bulk Cu density, the measured surface coverage, and the amount of Cu deposited. Variations in thickness are probably similar to the spread observed in cluster diameter as the contrast between clusters does not indicate large differences. The typical spacing between clusters is ~40 Å, with some separated by as little as ~10 Å. The isolated clusters show little apparent motion, even at room temperature, since there is no evidence of significant coalescence for 2 Å cluster deposition.

These results suggest that surface wetting occurs for Cu clusters on silica, resulting in thin flattened-disk shapes. Observations of Cu films grown by atom deposition on silica substrates at 300 K and higher temperatures have shown a tendency to ball up, even when the films are 500-5000 Å thick. This results in clusters that do not wet the silica, according to Young's formulation of wetting angles. However for clusters in our size range of tens of angstroms, the long range van der Waals forces must be considered in the expression of the contact angle.[20] Wetting of the Cu clusters here suggests that an attractive dispersion force exists.

In the absence of cluster-cluster interactions on the substrate, one would expect the surface to be covered in a Poisson-like distribution. For cluster deposition, we could examine the interaction of clusters by depositing clusters onto surfaces already decorated by clusters and investigating their spacing. For assembly by three consecutive depositions of clusters formed by 2 Å of Cu on Xe, the morphology represents a labyrinth, as shown by the lower image of Fig. 6. Elongated metallic lines are clearly visible with contrast that indicates variations in thickness around an average of ~10 Å. Although a few of the lines are isolated, most form part of a connected matrix. At the same time, there are open connected areas over 100 Å in size. The formation of a serpentine pattern cannot be accounted for simply by two-cluster sintering. Instead, rotations resulting from surface energy anisotropies, multiple cluster interactions, and cluster shape irregularities must occur to

Figure 5.

Schematic diagram showing Xe condensation on GaAs. Ag deposition onto the Xe buffer layer produces Ag clusters on the surface and isolated atoms that are trapped within the matrix. A layer of Xe coats the clusters to reduce the surface free energy. With time, the clusters are drawn through the Xe matrix until they contact the substrate. The springs represent the van der Waals force of attraction.

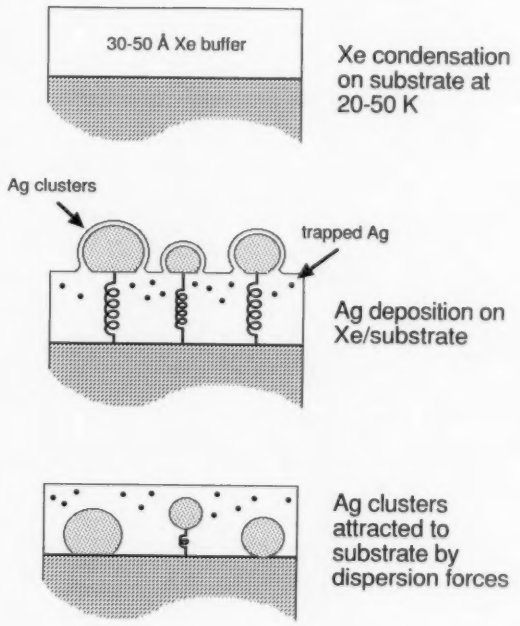
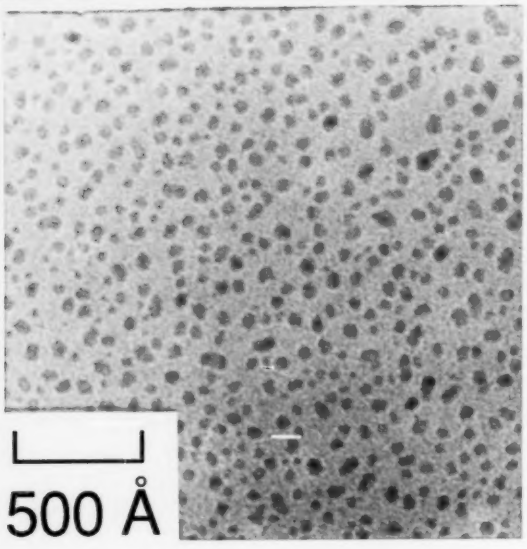
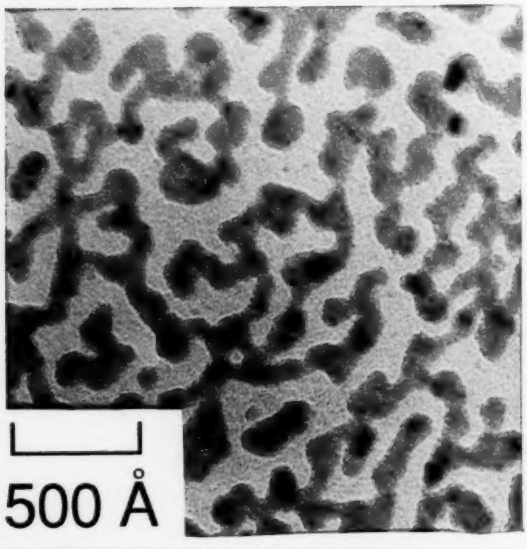

30-50 Å Xe buffer
Xe condensation on substrate at 20-50 K
Ag clusters
trapped Ag
Ag deposition on Xe/substrate
Ag clusters attracted to substrate by dispersion forces

Figure 6.

TEM images of Cu cluster assembly on silica. The upper panel for 2 Å deposition shows irregular clusters over ~25% of the surface (characteristic diameter ~40 Å). The lower panel shows the structure obtained by three successive 2-Å cluster depositions. Here, the interconnected Cu labyrinth covered ~60% of the surface (estimated thickness ~10 Å). The images showed little contrast after ten such cluster depositions.





form the larger open areas observed.[21] The observation of small enclosed areas within the Cu pattern demonstrates that nanocluster sintering may create voids similar to the pores observed in classical sintering.

When the deposition process is repeated in 2-Å increments to a total of 20 Å, the relatively uniform contrast in TEM suggests a homogeneous layer. From these results, we conclude that cluster assembly with small clusters formed on Xe will cover more than half of the surface after three depositions and all of the surface after 10 depositions. The complete coverage of the surface is important for interpretation of the interface photoemission results (and Schottky barriers for metal-semiconductor interfaces[14]).

Metal clusters on semiconductors

As discussed above, cluster assembly studies involving metal-semiconductor interfaces was motivated by an interest in creating an interface as gently as possible to simulate an ideal interface free of defects. We have used synchrotron radiation photoemission to investigate GaAs- and InP-based interfaces produced by cluster assembly. At low coverage, the clusters are widely dispersed across the surface because the individual clusters were isolated on the Xe prior to deposition. This is supported by TEM studies for Cu cluster assembly on silica surfaces. However, cluster coalescence becomes more likely as the amount of material deposited onto the Xe is increased.

The onset of metallic character for cluster-assembled overlayers has been investigated by studying the valence band evolution for depositions between 0.05 and 50 Å. In Fig. 7, we show photoemission energy distributions curves (EDCs) for Ag clusters deposited onto GaAs(110) at ~90 K. For direct comparison, we also show results for atom deposition onto GaAs(110) at 60 K. These spectra were acquired with synchrotron radiation using a photon energy of 65 eV. The bottom pair of EDCs is for the clean cleaved p-type GaAs(110) surface with 0.1 Å of Ag. Both spectra are dominated by emission from the Ag 4d-derived states ~5 eV below the Fermi level, E_F, because the photoionization cross section for Ag is so much greater than for GaAs at these photon energies. Features from GaAs are evident, however, at ~2.5 eV binding energy. For atom deposition at 60 K, film growth occurs in a layer-by-layer fashion. The photoemission results show that the Ag d-bands representative of metallic Ag are not completely developed until ~5 Å. In contrast, the photoemission results from clusters deposited directly indicate that the Ag d-bands are fully developed by 1Å deposition and the spectra are characteristic of the metal. For cluster assembly, the persistence of emission from the GaAs substrate at ~2.5 eV below E_F (Fig. 7) also demonstrates that the substrate is only partially covered by clusters. With increased cluster deposition, the fraction of exposed substrate is diminished.[14]

Figure 7.

Representative valence band spectra for Ag cluster deposition (right) and Ag-atom deposition at 60 K (left). For atom deposition, the Ag d bands gradually broaden to their full metallic width by ~5 Å. For cluster deposition, this width is already achieved by =1 Å. This demonstrates, similar to Fig. 4, the metallic character of the clusters even for relatively small coverages.

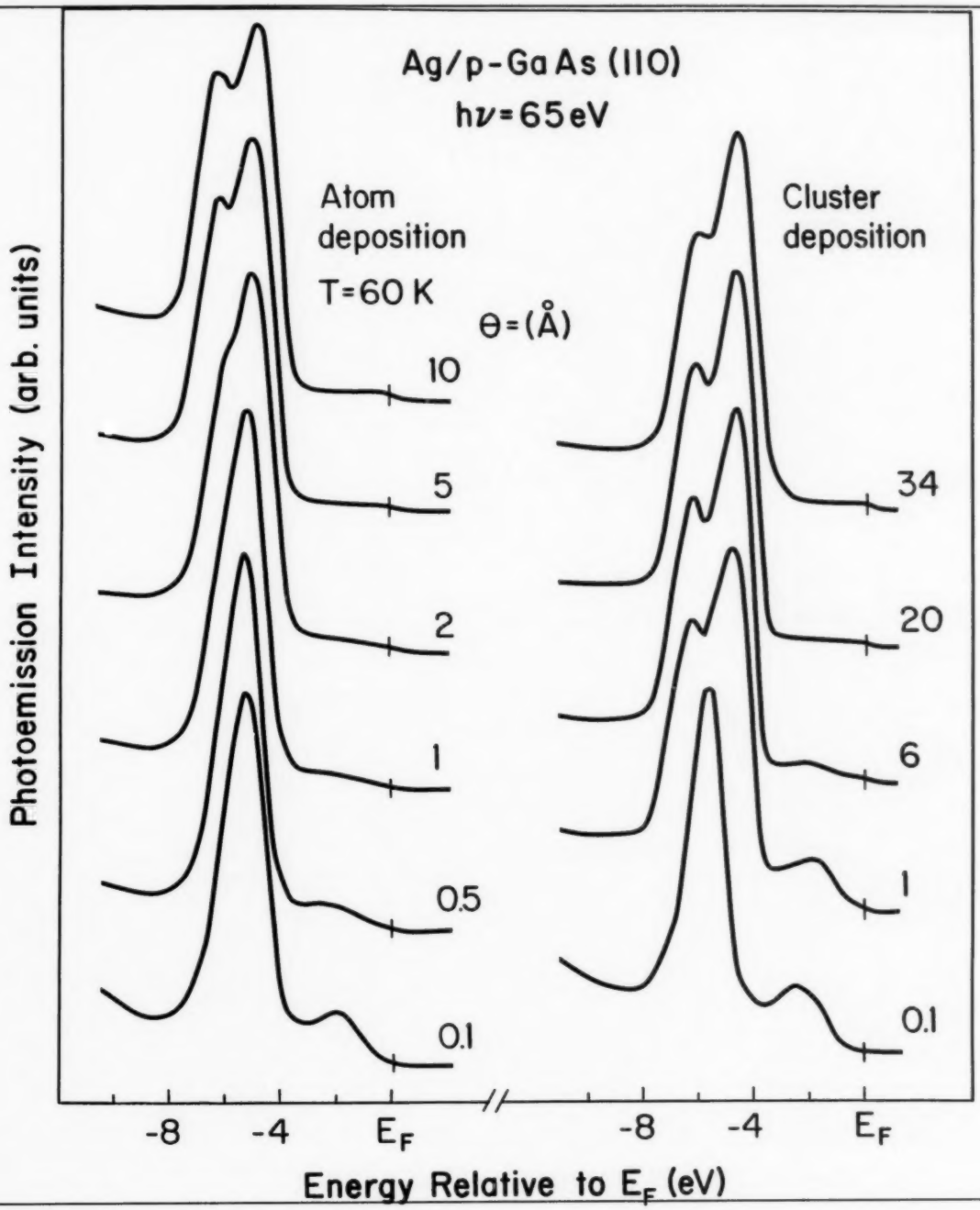
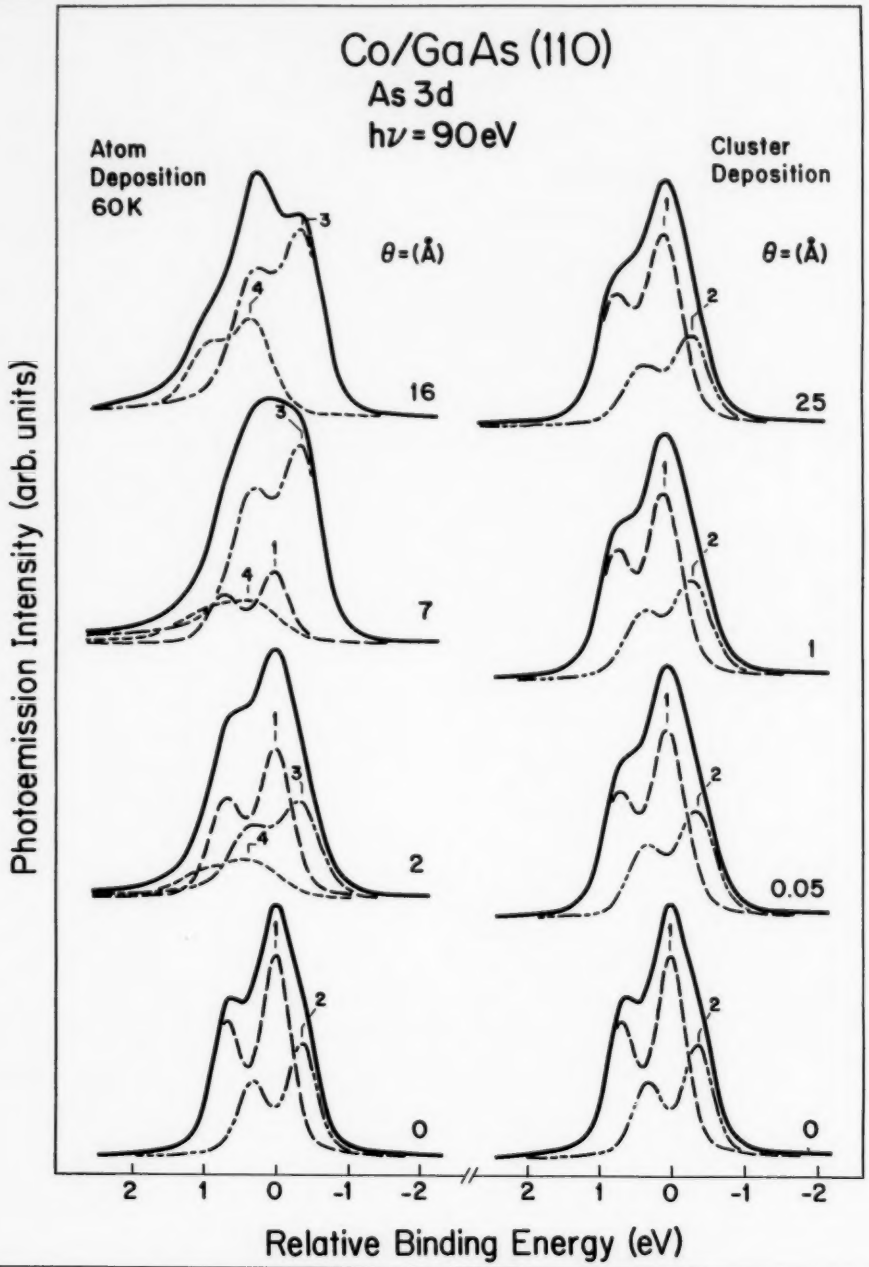


Figure 8.

Representative As 3d core level EDCs and lineshape decornpositions for Co-cluster deposition and for Co atom deposition at 60 K. Components 1 and 2 correspond to emission from bulk and surface As atoms. Components 3 and 4 are induced by atom deposition at 60 K and correspond to As atoms released from the substrate. Cluster deposition alters the relative intensity of the surface and bulk components but introduces no new spectral features.

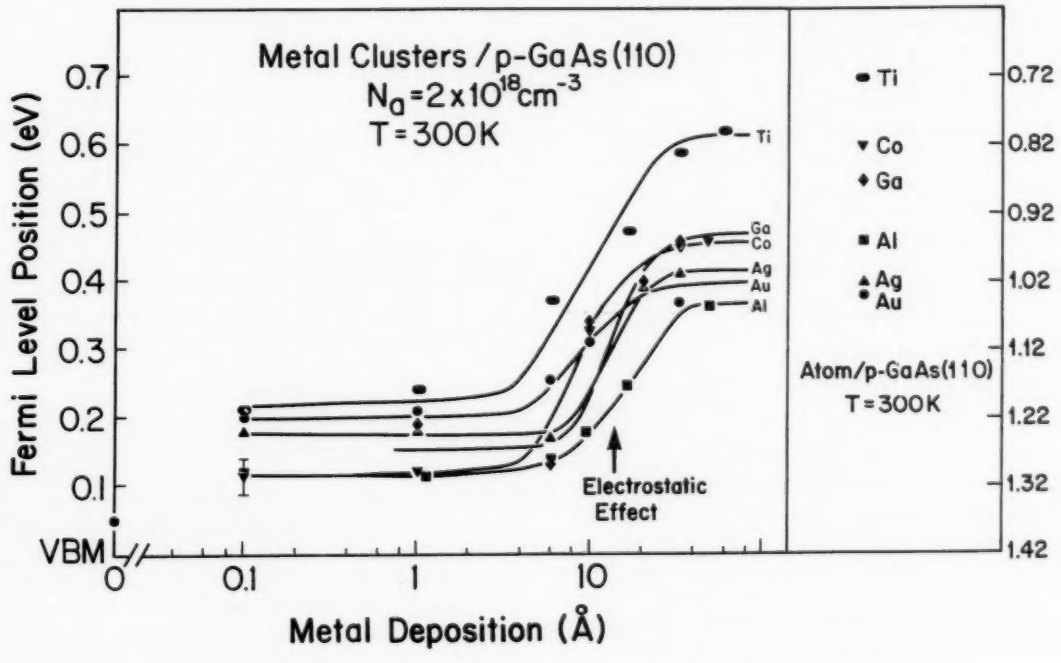


The nature of the contact between the cluster and the semiconductor surface is of particular interest. Core level photoemission is the technique of choice to investigate chemical changes associated with reaction even though the clusters quickly become thick enough to prevent the escape of photoelectrons from the substrate. In Fig. 8 we show representative As 3d core level spectra taken at hυ = 90 eV (photoelectron mean free path of ~4 Å) for Co cluster deposition (right) and atom deposition at 60 K. For the clean GaAs(110) surface, the As (and Ga) 3d EDCs include contributions from atoms at the relaxed surface (labeled 2) and in the bulk (labeled 1). The ratio of the intensities of components 1 and 2 is an indication of the surface sensitivity of the measuring technique. For Co cluster deposition on GaAs(110), the only lineshape changes correspond to a slight increase in the Gaussian width and a decrease in the emission intensity from surface-shifted atoms (feature 2) relative to that from bulk atoms (feature 1). The increased Gaussian width is due to the fact that the measurements for the clean surface were done at 60 K while those following cluster deposition were done at ~300 K, i.e. thermal broadening. The relative intensity changes are important in understanding the electrical properties of the interface. It is important to note that no adsorbate-induced features are required to fit the core level spectra. This conclusion for Co(clusters)/GaAs(110) is also valid for a wide range of different metal cluster overlayers on GaAs(110).[14]

Examination of the As 3d core level spectra following Co atom deposition shows dramatic lineshape changes, in contrast to the cluster assembly results. The two components that dominate the spectra for depositions above ~2 Å are due to As atoms released from the substrate.[1] In this case, the released As atoms tend to segregate to the surface region of the thickening Co overlayer, as indicated by the persistence of emission for thick metal coverages. Component 3 can be identified with As atoms at the surface while component 4 arises from As atoms within the Co matrix near the surface. The redistribution

Figure 9.

Fermi level position as a function of metal-cluster deposition on lightly doped n-type GaAs(110). The energy positions are almost independent of metal and coverage with a very gradual shift ot a position ~0.32 eV below the CBM. The average error bar corresponds to 0.03 eV. We emphasize that the scatter in data points for the six different metals is remarkably small compared to the measurement accuracy. These values are independent of temperature, except for Ti, which, as discussed in the text, reacts spontaneously. Each point corresponds to a complete experiment beginning with a fresh cleave. For the clean surface, E_F fell within 60 meV of the CBM.



of the released atoms depends on whether alloy- or compound-like structures can be formed and the solubility of the atoms in the overlayer, with nonequilibrium distributions for growth at 300 K, and even more so for low-temperature growth. These processes are common at interfaces grown by conventional atom deposition.[1] What is remarkable is that they are not observed at interfaces grown by cluster deposition.

For the clean GaAs(110) surface, there are no surface states within the band gap and E_F is located very near the valence band maximum (VBM) or conduction band minimum (CBM) depending on doping types. In particular, Ga and As 4p states that would be in the gap for the ideal surface are swept out of the gap by surface relaxation. When a metal overlayer is formed, a potential energy barrier develops due to the creation of gap states near the semiconductor surface and there is a redistribution of charge. This Schottky barrier produces the rectifying properties of these junctions. Despite years of study, the precise nature of these states remains controversial.[1]

For metal overlayers grown by conventional atom deposition methods, the position of E_F at the surface depends on coverage, with gradual movement into the semiconductor band gap after deposition of a few monolayers. The final E_F position, and the coverage at which it is reached, depends somewhat on the metal overlayer itself. In contrast, cluster deposition produces a barrier height that is nearly independent of coverage and overlayer metal. This can be seen from Fig. 9 where we show the Fermi level position relative to the CBM as a function of cluster deposition of Ag, Al, Au, Co, Ga, and Ti on n-GaAs(110). For the cleaved surface, E_F is within 60 meV of the CBM, but it moves to ~260 meV below the CBM for depositions as low as 0.02 Å. Thereafter, it moves gradually to a position ~320 meV below the CBM. For 35 Å deposition, ~90% of the substrate has been covered by clusters and it seems unlikely that E_F will move much further. For these same metals, the final Fermi level position for atom deposition varies from 0.6 eV below the CBM for Ga to 0.9 eV below the CBM for Au. It is therefore quite surprising to observe a pinning position for cluster deposition that is so high in the band gap, that exhibits so little coverage dependence, and is independent of the metal.

The results of Fig. 9 can, however, be understood by recalling that the only change in core level lineshape observed following cluster deposition was due to a decrease in emission from the surface atoms relative to the bulk atoms (for example, Fig. 8 for Co). The existence of the emission feature from surface-shifted atoms is due to differences in charge occupation of the surface dangling bonds relative to the bulk bonds and to the surface relaxation. Thus, the change in the relative intensity of emission from the surface-shifted and bulk substrate atoms at the cluster-assembled interface is probably due to a loss of the surface relaxation around the cluster perimeters. This would result in the reappearance of intrinsic states within the semiconductor gap that would pin E_F, in agreement with the experimental results.

The Fermi-level movements of Fig. 9 are due to energetic processes involved in cluster-assembly rather than simply to the cluster morphology at the interface. For example, we have shown that large clusters are formed when Ag is deposited on GaAs(110) at 300 K in an atom-by-atom method.[14] Although cluster deposition also gives clusters, the final Fermi level positions are quite different for the two Ag(clusters)/GaAs structures.[14] The fact that energy is dissipated by the GaAs substrate for atom deposition but is dissipated by the Xe film for cluster deposition indicates that such energies play a critical role in the properties of the interface.

Concluding Remarks

This paper has focused on the formation of clusters at surfaces during atom deposition. We have shown that clustering is a common event, and we have shown that STM is a particularly important technique to demonstrate their character. We have shown that it is possible to eliminate certain processes that occur during conventional methods of interface growth simply by eliminating contact between the two materials until bulk-like properties are developed for both. The gentle joining associated with cluster assembly circumvents the dissipation of energy derived from processes such as adatom impact, bonding, and coalescence directly on the substrate. The prospects of forming abrupt or nearly-abrupt interfaces are not limited to semiconductor-based systems, nor are these the only systems for which such interfaces are desirable. Indeed, cluster-assembly can be more generally applied to any system. One of the most stringent tests of the technique has involved the assembly of clusters on the high-temperature superconductors where there are strong driving forces for intermixing. In this case, the opportunity to create a boundary by solid-solid assembly was particularly attractive because the loss of superconductivity is associated with substrate disruption. In principle, these interfaces are more suitable to theoretical modeling of processes and properties, and they have demonstrated properties substantially different from conventional interfaces. Studies involving cluster assembly[17] have demonstrated greatly suppressed surface modification, as expected based on the fact that the clusters behave differently on the surface.

It should be emphasized that investigations into controlling and altering interface properties with cluster assembly are very recent, and the understanding of these interfaces is still in its infancy. As far as future studies are concerned, cluster assembly will make it possible to address a number of issues concerning surface magnetism, catalysis, and compound growth. It will be possible to produce isolated magnetic clusters so that the fundamental properties of these systems and their interactions can be investigated. Cluster-assembled interfaces can also be used as model catalysts, and the properties of molecular chemisorbed species on these clusters can be probed. Intriguing issues concerning surface wetting and cluster sintering can be addressed

by growth of clusters and nanostructures. Finally, it will be possible to address fascinating issues involved with the transition from atomic-like materials to bulk solids by studying the properties of different sized clusters, synthesized by variations on the techniques described.

Acknowledgments

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Biography

Professor Weaver received his B.S. and Ph.D. degrees in Physics from the University of Missouri and Iowa State University in 1967 and 1972, respectively. He was a member of the scientific staff at the Wisconsin Synchrotron Radiation Center from 1973 until 1982 when he moved to the University of Minnesota to develop the electronic materials thrust area. His research focuses on the physics and chemistry of interfaces, using and developing the technique of surface science to investigate evolving overlayers grown on a wide variety of surfaces. Common to much of his work is the interest in changing the growth parameters, including the temperature, the ionization states of the adatoms, and the chemical species of the overlayer and substrate. He developed the cluster-assembly technique to alter the interactions at the boundary.

Professor Weaver has been supported by ONR since 1984. He is the author of approximately 325 refereed papers and chapters, including features articles in Scientific American, Physics Today, and Science.

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Nanochemistry and Nanoclusters: The Beginning of Matter

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Introduction

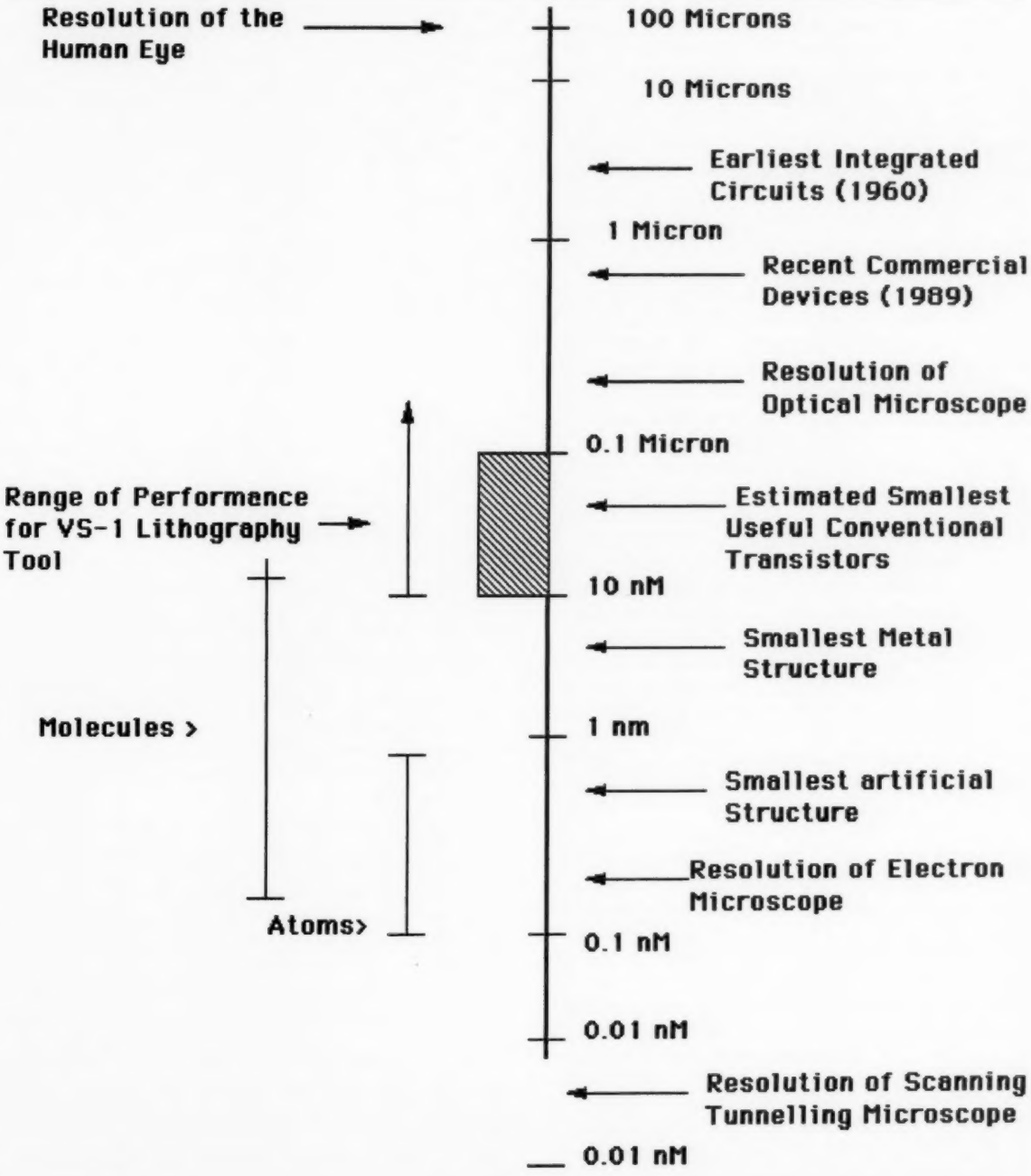
Ultimately all materials and living organisms have their origins in the collective assembly of a small number of atoms or molecules. Whether it be the beginning of life, crystallization, or the natural formation of a complicated nanocomposite like a sea shell, this is a fascinating process because it is at this stage that the inherent future properties such as shape, mechanical strength, color, conductivity, etc. are established. It is also a time when the atoms or molecules are not certain as to whether they would prefer to be associated as an array or nano (a dimension on the order of atomic radii, 1 nanometer = 10^{-7} cm) cluster or on their own in the surrounding environment. Physically this simply means that the intermolecular and interatomic interaction energies associated with the self assembly are of the same order of magnitude as the attractive energy that the atoms or molecules have for their surroundings. The chemistry of this nucleation process is therefore particularly sensitive to changes in composition and external effects such as temperature, electric fields, or anything that even slightly perturbs the dynamics and kinetics of the system.

Why are arrays of atoms in this size regime important? In biological systems, for example, it means that the atoms that make up the cluster are readily accessible and can be efficiently used. The iron that our bodies need so badly is provided via an iron transport cluster entity called ferritin[1-3]. Ferritin consists of a shell of proteins which surround an iron core of up to 4500 iron atoms that is essentially spherical with a diameter of 80 Å. The composition approximates closely to $(FeOOH)_8$ $(FeO{\bullet}H_2PO_4)$. In fact, the iron core has a close structural resemblance to ferrihydrite, an iron oxide bulk solid $(5Fe_2O_3{\bullet}9H_2O)$[4] that contains a close packed array of oxide and OH^- ions with iron atoms in octahedral interstices. Obviously it is not in the best interest of our bodies for the 4500 iron atom cluster to expand, i.e. to continue to crystallize, into several grams of ferrihydrite with ~10^{23} atoms. Somehow nature provides a way to stop the growth at 4500 atom irons and to package these atoms in a useful way. In this case, phosphate $(PO_4)^-$ groups in ferritin cap and passivate the exterior surface.

The surfaces of nanosized clusters must either have considerable curvature or else abrupt changes in shape. During catalysis, this means that the atoms on nanosized clusters are more exposed than those in larger particles, making them much more reactive towards other chemical species. On the other hand, this exposed atom reactivity also means that the

Figure 1

Fabrication of structures and devices whose dimensions are less than a few millionths of an inch (1 micron - 40 millionths of an inch). The author acknowledges IBM Research Laboratory for this figure.



clusters are not very stable and can either join with neighboring clusters or be poisoned with respect to the catalytic process by other reactions.

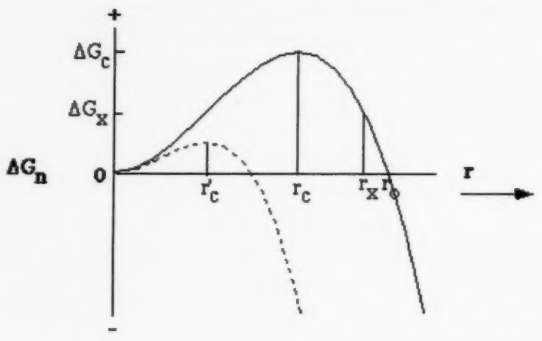
A third area where nanocluster materials have a significance and impact is in photonic/electronic applications. The miniaturization of electronic and optic devices has revolutionized response times, energy loss, and transport efficiency (Figure 1). Additionally, the presence or absence of a few atoms and the geometrical disposition of each atom can significantly modify electronic and photonic properties as one approaches the nanosize regime. This control can be further supplemented by "packaging" assemblies of atoms or molecules into thin film or nanocomposite bulk materials to define surface states, cluster environment and geometry, intercluster interactions, and consequently, a wide tunable range of optical and charge carrier responses.

Utilizing nanoclusters in photo-optics has attracted considerable commercial interest (See inside cover figure). Collimation of a laser beam to get the highest possible optical density in writing on a optical disk is limited by diffraction effects if collimation is used to attain a small laser beam diameter. We also see that the intensity of the laser beam is not homogeneous in cross section which also restricts the resolution and sharpness of reproduction. Nanosized semiconductors display a peculiar nonlinear optic property: they will absorb light if it is not too intense, but will transmit light if the number of photons surpasses a certain threshold value. By using a thin film mask containing the semiconductor clusters, only the center portion of the beam, which has a photon flux above a certain intensity cutoff, is transmitted, dramatically (~50%) improving both optical density and recording quality. Using shorter wavelengths further improves the resolution. Fortunately, the optical absorption and emission bands of a semiconductor shift to shorter wavelengths if the semiconductor atoms are in an appropriately small cluster. If these effects are observed, the electrons in the semiconductor are said to be quantum confined, and the semiconductor is sometimes referred to as a quantum confined material.

Quantum confined materials are creating numerous opportunities to develop new science and technologies. Research on electro-optic (EO) and nonlinear optic (NLO) processes began in earnest in the early 1960's after the invention of the laser so that the topic of nonlinear optical materials is just beginning to reach the mainstream of chemistry. However, when one realizes the possibilities for decreasing computing times with optical computers, increasing our capabilities to manipulate and store visual images using thin panel optical display devices, forming optical neural networks involving "thought" processes similar to those of our own brains, and a host of other applications, the reason for excitement about this rapidly growing field becomes clear. Optical data transmission can be accomplished with less energy loss and device heating. In addition, optical signal transmission is much less vulnerable to disruption by external electromagnetic fields or other radiation sources. It has been suggested that the former of these effects will lead to desk top Cray computer capabilities within the next ten years.

Figure 2.

Variation of free energy of nucleation with cluster radius during synthesis. r_c is the kinetic critical radius and r_o is the thermodynamic critical radius. For the solid line the surface and bulk free energy contributions are assumed to be the same, while for the dashed line the bulk free energy is assumed to be twice as large as the bulk free energy.



Many other examples could be cited. A bottom line is that classical laws become unreliable as the dimensions become smaller and smaller. This applies not only to electro-optic phenomena, but also to mechanical concepts, such as friction, fatigue, and stress. Yet, IBM researchers have shown that near 0°K it is possible to arrange 35 xenon atoms into an array which spells out the IBM logo by manipulating individual atoms with a scanning tunneling microscope tip. It is a very exciting and unpredictable frontier between the classical and the quantum world.

Because of the importance of nanocluster chemistry to a wide variety of fields, ranging from atom and electron transport in biological systems, heterogeneous catalysis, photo-catalysis, to the development of new electro-optic devices based on quantum confinement, there has been an explosion of interest in this area by scientists from many areas. Nanocluster syntheses have been carried out in numerous ways to give unexpectedly different materials with varied structural, optical, and transport properties. Molecular inorganic, physical, and biochemists have generated nanoclusters by building up arrays from solution or gas phases atom by atom.[5-7] From the other directions, solid-state physicists and engineers have focused on increasingly smaller and smaller dimensions with engineering based directly on a solid-state atomic lattice substrates.[8,9] *The materials chemistry at this molecular and solid-state interface requires a precise definition of the number of*

atoms, their siting (e.g. bulk versus surface), and ultimately the manner in which they are assembled on the surface and within the cluster to form a nanocomposite array. It is for these reasons that while the convergence of molecular and solid-state chemistry is near, the somewhat diffuse materials synthesis interface between isolated clusters and the infinite solid array is only beginning to be resolved.

This article is concerned primarily with nanocluster packaging. In order to demonstrate why packaging is important, we will first briefly review the thermodynamics associated with cluster synthesis by the assembly of atoms through nucleation.

Nucleation and Critical Radii

Nucleation means change. The system of interest has been perturbed in some fashion so that thermodynamically it is no longer at equilibrium. In order to induce nucleation we may lower the temperature to decrease solubility or increase the concentration of the particle that we wish to nucleate. We also can change the solvent medium so that the solvation energies are decreased, which will in turn result in interparticle interactions becoming dominant.

For any process to proceed spontaneously, the free energy for the change, ΔG_n, where n refers to the nucleation, must be < 0. Assume that the species are randomly ordered at the beginning, which is usually the case. Since the disorder of the system decreases during nucleation, the entropy contribution to the free energy change will be unfavorable (< 0) and becomes increasingly so with increasing temperature.

The driving force for the nucleation is the attraction of the atoms or molecules for each other. Ordinarily this attraction is three dimensional, and is accompanied with a decrease in free energy per unit volume, $-\Delta G_v$. Therefore, for a spherical cluster of radius r, the gain in free energy is $-(4/3)\pi r^3 \Delta G_v$. Assuming that we have adjusted the temperature, solvation effects, and other factors that would favor the isolated nuclei, what prevents nucleation from occurring? Clusters have surfaces, and associated with these surfaces is a surface energy which makes a positive contribution to the nucleation. One way to view this effect is that the atoms at the surface interact more strongly with their neighbors than do the atoms in the bulk. In a sense the surface must be weakened and possibly rearranged in order to continue the cluster growth. Denoting the surface free energy change per unit area of the cluster as ΔG_s, the net change in free energy during nucleation is:

$$\Delta G_n = 4\pi r^2 \Delta G_s - (4/3)\pi r^3 \Delta G_v \qquad (1)$$

This relationship is plotted in Figure 2 and reveals several key points. The most important point for our purposes is the critical role that the surface plays in the process of forming a cluster. Initially the overall free energy for the nucleation is positive, but with increasing radius of the hypothetical spherical cluster, ΔG_n passes through a maximum ΔG_c when the cluster has a radius r_c. As the radius increases, ΔG_n decreases to zero and first becomes negative for $r > r_o$. The significance of this can best be seen by considering the fate of a small cluster with radius r_x. Thermodynamically this cluster is unstable since $\Delta G_x > 0$. However, if it were to start to dissolve, its radius would decrease and the free energy would become even greater so that it is kinetically stable. We conclude that clusters with a radius $r < r_c$ are going to continue to grow. Nuclei with radii $r_c < r_x < r_o$ are called metastable since they require an activation energy ($\Delta G_c - \Delta G_x$) for their dissolution. Clusters with radii $r < r_c$ are unstable since there is no barrier to their dissolution. Clusters with radii $r > r_o$ are over the hill, i.e. stable, since growth to larger clusters is then both kinetically and thermodynamically favored.

So how can we stabilize smaller clusters or possibly intercept clusters with an arbitrary radius? One way is shown by the dashed line in Figure 2. Here $\Delta G_v = 2\Delta G_s$ while for the solid curve it is assumed that $\Delta G_v = \Delta G_s$. Clearly if we can increase the binding energy between our atoms in the bulk relative to the surface energy, smaller clusters will be more stable. Another alternative is to "package" the clusters. Chemically this means that as a cluster is forming the atoms on the surface of the cluster will be capped and passivated with respect to further growth. This could be done either by simply adding a passivating reactant to the nucleation media or by growing the clusters within a protein or inorganic cavity, the walls of which contain the passivating groups. Both of these approaches are described below. We begin with molecular or polymeric packaging.

Growing and Packaging Molecular Clusters

Unreactive and Reactive Cluster Surfaces

As described in this issue's accompanying articles by Smalley and Weaver, it is now possible to synthesize a variety of clusters of specific size and shape by high-vacuum vapor phase techniques. In a few cases, such as for the remarkable C_{60} Buckyball, it has been possible to develop macroscopic synthesis techniques to create relatively large quantities of solid-state materials which contain the same carbon cluster. This is possible because of the stability of the closed electronic shell structure obtained by the carbon atoms on the surface of the Buckyball. Their arrangement is similar to that in graphite with aromatic delocalized bonding through alternating C-C and C=C bonds with no "dangling" bonds, i.e. the Lewis octet rule is satisfied for all the carbon atoms. In terms of the thermodynamic model described above, ΔG_v is defined by the formation of a closed surface with anisotropic bonds within the surface. The alternative of a fragment of a graphite sheet with dangling radical bonds is less favorable.

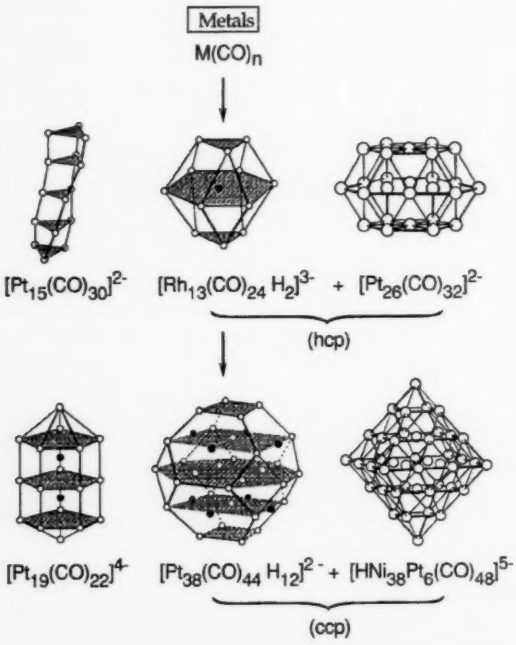
Metal Clusters

Apparently metals also can form resonance bonding of this type, but not to the extent of being able to exclude reaction at the metal cluster surface. For example, Schmid has reported a family of clusters based on the closest packing of heavy Au and Pd atoms to give "magic" numbers of 13, 55, etc. with the nth shell containing $10n^2 + 2$ atoms. These include $Au_{55}(P(Ph)_3)_{12}{}^{6+}$ (Ph = C_6H_5) and $Pd_{561}(phen)_{36}O_{190\text{-}120}$ (~26 Å in diameter with 5 spherical shells, and phen = phenanthroline).[10] Isolation and characterization of a pure phase of the latter has not yet been reported. The largest metal-metal bonded nanocluster which has been synthesized and structurally characterized by single crystal diffraction measurements is $[HNi_{38}Pt_6(CO)_{48}]^{5-}$.[11] These are excellent examples of the "passivating reactant" approach described above used for the stabilization of clusters. More graphically, they can be viewed as small chunks of metal which are solubilized by a coating of ligands (phenanthroline, CO, $P(Ph)_3$).

Studies of these metal nanoclusters have beautifully demonstrated the fact that the bonding at the exterior surface of the cluster can energetically dominate the ultimate cluster geometry. The dimensions of these fragments are large enough so that one observes both hexagonal and cubic close packed arrangement of metal atoms in $[Pt_{26}(CO)_{32}]^{2-}$ and $[Pt_{38}(CO)_{44}H_x]^{2-}$ clusters respectively.[12] However, in $[Pt_{15}(CO)_{30}]^{2-}$, the platinum metal atoms arrange themselves in a helical array of triangular Pt_3 units and in $[Pt_{19}(CO)_{30}]^{2-}$ the metal cluster is a bicapped pentagonal-prism similar to the geometry reported for certain microcrystalline materials such as metal dendrites and whiskers.[13] These geometries are still an unresolved challenge to theoretical chemistry as well as to the development of useful predictive theories for nucleation phenomena.

Figure 3.

Isolated capped metal atom clusters. Note the hexagonal closest packing (hcp) and cubic closest packing (ccp) arrangements even for clusters of this size.



Semiconductor Clusters

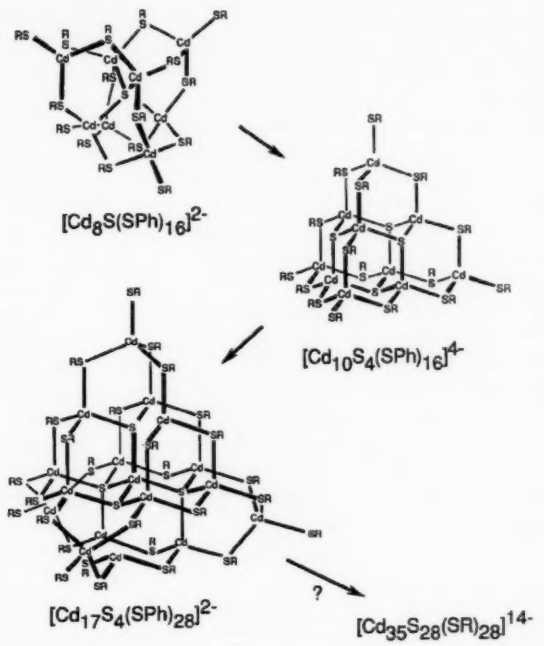
Approach and Background

Even more so than for metal clusters, resonance and delocalized bonding are not available to stabilize the cluster surface for inorganic materials such as semiconductors or the ferritin clusters described above. The atoms on the surface of the cluster for these classes of materials are highly reactive and without exception need to be stabilized, either by coordinating molecules which block the surface or by atoms which provide the necessary electrons for an inert gas configuration. In practice this means that given the opportunity the cluster will either continue to add more of the same atoms to give further cluster growth or will react with the atoms and molecules in the immediate environment. The size of the cluster that is synthesized is, therefore, determined by (1) the strength of interaction of the capping ligand to the surface relative to the bulk atom-atom interactions and (2) the kinetics associated with the competition between cluster growth and capping. For example, if the growth media is saturated with the capping ligand, the probability of cluster growth is minimized even though it may be thermodynamically favored.

The chemistry needed to generate nanoclusters is indeed state-of-the-art, requiring control of kinetic parameters beyond the limits of that which have been previously achieved in solution chemistry.[14] The goal is essentially to arrest a runaway reaction, which if given sufficient starting materials will result in the generation of a bulk material. The appropriate cluster size is achieved by competitive reaction chemistry between core cluster growth and surface capping which terminates the cluster growth. This kinetic control is obtained by adjusting the reactant concentrations, diffusion rates, temperature of reaction, choice of solvent, time of reaction, and the use of microheterogeneous reaction media. Cluster growth is then terminated by the use of strong coordinating ligands.[15-17] For small clusters (8-15 Å), which are soluble in organic solvents, a single size can be obtained either during synthesis or by separation after synthesis. For larger clusters the kinetics of the nucleation and passivation processes are fast and in

Figure 4.

Molecular semiconductor clusters of cadmium sulfide.



general a typical preparation gives a poly dispersity of ±10% in particle diameter.

What Size?

The first question that needs to be addressed in nanoclusters is obviously the desired size of the cluster. In principal, such size can be arbitrarily adjusted. Because of the many potential applications, semiconductor clusters in which the electrons are quantum confined are highly desirable. A brief definition of quantum confinement is, therefore, in order.

Quantum confinement arises when a photon with energy equal to or greater than the energy gap ($h\upsilon > E_g$) of a semiconductor induces an electronic transition from the valence to the conduction band. Spatially the electron moves from an atomic site through the lattice via the conduction band orbitals. The positive charge left behind is appropriately called a hole and is weakly bound to the electron over relatively large distances (~100 Å). This bound electron-hole pair is called an exciton. It is easier for the electron to delocalize through the lattice if the valence and conduction bands are close in energy since thermodynamically there is not as much to be gained for the electron to recombine with another hole. For this reason the distance of the electron from the hole is inversely proportional to the band gap, E_g.

To a first approximation the exciton can be viewed as the analog of a simple Bohr hydrogen atom. The electron orbits around the positive charge in the lattice at distances on the order of 20-300 Å depending on the band gap. Quantum confinement occurs when the individual clusters of the semiconductor are the same size or smaller than the exciton radius. The electron finds that it is not free to move as far away from the hole as it would like and the motion of the weakly bound electron-hole pair becomes quantized. The size of the cluster required for quantum confinement in a small bandgap semiconductor such as InP (E_g = 1.27eV) is on the order of 400 Å since the exciton electron-hole separation is about this large, while that for a large band gap semiconductor like CuCl (E_g = 3.1 eV) is only ~ 14Å. In general, unusual optical and electronic properties will be evident at or below these respective radii for these materials.

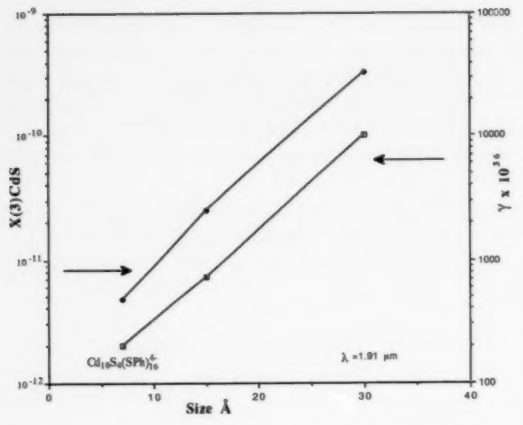
An Example - Group II-VI Atoms

A good example of the application of this approach to molecular cluster packaging is provided by recent studies of cadmium sulfide. Dance has created soluble molecular clusters such as $[C_{10}S_4(SPh)_{16}]^{4-}$ (Fig. 4, Ph is a phenyl group, C_6H_5) which can be considered as fragments of the bulk semiconductor lattice.[18-20] As molecular entities these are soluble in organic solvents so that they can be isolated and structurally characterized, with the largest structurally characterized cluster reported to date being $[Cd_{17}S_4(SPh)_{28}]^{2-}$.[21] This structure contains tetrahedrally coordinated Cd and S atoms as does bulk CdS, however, each Cd atom also is bonded to a surface S atom which is part of the -SPh thiophenol group. This manner of covalent bonding at the surface provides the passivation necessary to control cluster aggregation and gives a monodisperse size. Notice that the ratio of Cd:S in this material is not 1:1 but approximately 1:2. This nonstoichiometry is common among small particle semiconductors as will be discussed for GaP included in zeolites in the next section. As illustrated in Figure 4, a variety of nanocluster geometries are possible.

Although this review is directed primarily towards nanocluster chemistry, it is useful to ask whether these very small semiconductor atom fragments have any potential in optical applications. The optical disk storage example in the introduction has a substantial 3rd order non-linear optic response, which in turn implies a high degree of polarizability of the atoms. The strongest nonlinear response to incident light occurs at resonant frequencies; natural frequencies for transitions between quantum states. At these frequencies, transitions to higher energy rotational, vibrational, or electronic states lead to large charge displacements. This has meant that in the search for large optical responses, resonant or near resonant optical frequencies have been used for the light signal carrier. Unfortunately, at or near-resonant frequencies, photons are no

Figure 5.

Nonresonant 3rd order nonlinearity of quantum confined CdS clusters.



longer weakly perturbed as they travel through the optical medium; non-radiative decay from the high-energy or excited states to the ground state can result in sample heating and loss of photon efficiency. If the photons are being used as optical signal carriers, these loss factors can be disastrous. Ideally, one would like to create optical materials for electro-optic device applications which could be used at non-resonant frequencies with no photon dispersion.

Cheng, Herron and Wang[22] have demonstrated that the very small clusters, shown in Figure 5, have large nonresonant nonlinearities (Figure 5). In fact, the Dance compound has a nonresonant nonlinearity comparable to that of conjugated organic dye molecules and bigger clusters have even larger nonlinearities. This strongly suggests the possibility of using semiconductor nanoclusters in relatively loss-free data transmission or electro-optic photonic devices.

Packaging The Clusters In Solids – Nanocomposites

With very few exceptions, the isolated molecular nanocluster is only part of the story. For most practical applications, the nanoclusters must be incorporated into a processable matrix. We will call this combination of a host matrix and the guest nanocluster a *nanocomposite*, indicating a material consisting of two or more phases with different physical properties that are interfaced at nanoscale dimensions. The nanocomposite can be constructed (1) directly by synthesis, (2) by first creating the host and then carrying out nanocluster synthesis within the host, or (3) by creating both host and guest and then diffusing the guest into the host. For frequency conversion or optical bistable devices, such as the optical disk example above, a high-optical density is required with the nanoclusters closely packed. The nanoclusters will then be separated at distances comparable to their own dimensions. The figure of merit parameters that might be used to optimize a nanocomposite are defined by the intended application.

In order to take maximum advantage of the unique properties associated with nanoclusters, the packaging must maintain a precise definition of the number of atoms, their siting (e.g. bulk versus surface), and the manner in which they are assembled to form a nanocomposite array. A compromise will sometimes be commercially necessary for processability or materials cost advantage, and for some applications the figure of merit criteria could be met with this in mind. The following discussion briefly reviews the types of host matrices that have been used for amorphous host and layer (1-d) packaging, and then continues along the lines indicated above, namely with the intent of seeking the most precise ways of packaging quantum confined semiconductor clusters *in a 3-d array*. Ideally this packaging would result in a nanocomposite that would include:

- size and topographical uniformity of nanoclusters
- 3-d periodicity
- tunability with respect to atomic modification of
  - topography
  - cluster dimensions
  - surface states defined by the cluster/packaging interface
  - intercluster coupling
- thermal and optical stability
- optical transparency

Amorphous Hosts

Porous glasses[23], polymers[24], micelles[25], and colloids[26] have been used as host matrices. Specific examples include the formation of PbS particles on ethylene-methacrylic acid copolymers[27], and glass matrices around colloidal solutions of CdS.[28] In all of these systems, however, the crystallinities, pore sizes, and ultimate cluster geometry are not well defined Nevertheless, porous glasses are promising in that they offer the advantages of having a large range of pore sizes, ease of optical characterization, and the potential for use as thin monoliths in optical devices. Photo and thermal stability are crucial if the nancomposites are to be used in laser device applications. For example, in optical computer or optical switching applications, the nanocomposite should be able to perform trillions of switching operations/sec for years at a time. As inorganic hosts, porous glasses have been demonstrated to greatly increase the lifetime of organic dye lasers

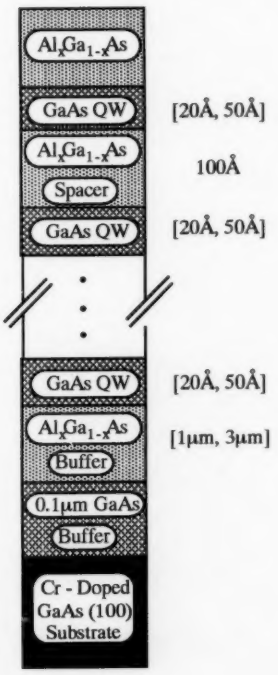
which have been built into their pores.[29] This is an important property of the inorganic host/organic guest combination that will undoubtedly be pursued further. Several types of sol-gel derived glass have been used in attempts to vary the size of the particles which are produced. In addition to the sol-gel derived glasses, commercial Vycor (Corning Glass) has been used. Vycor is significantly stronger than the sol-gel derived glass since it is synthesized via a high-temperature acid leaching process of borosilicates. The high temperature imparts mechanical strength to the glass.

Layered Synthesis and 1-d Confinement – Ordered Arrays

Sophisticated techniques currently are available to obtain 1-d confinement of atomic or molecular monolayers (~5Å) by molecular beam epitaxy (MBE), electrochemical, atomic layer epitaxy (ALE)[30] and Langmuir Blodgett film synthesis.[31,32] Molecular beam epitaxy (MBE) and atomic layer epitaxy (ALE) allow for the fabrication of ultrathin- (monolayer) semiconductor layers, and have lead to the design and creation of 1-d quantum confined materials. Figure 6 shows how carrier confinement is achieved by sandwiching a GaAs semiconductor layer between two wider-bandgap semiconductor epitaxial layers.[33-35]

Figure 6.

Molecular beam epitaxy derived quantum superlattice.



The superlattice layered structure approach is an important step towards achieving the degree of sophistication required to obtain a periodic array of quantum confined planes of atoms. However, the development of photonic transistors or other electronic device analogs requires 2-d (quantum wires) and 3d (quantum dots) confined structures. Some ingenious approaches to this problem using tilted superlattices have been partially successful but are challenged by the difficulty in obtaining the necessary precision to create lateral surfaces for boxes or walls with dimensions less than ~100Å.

3-d Surfaces and Periodic Packaging

The above discussion describes the generation of isolated clusters and the formation of superlattices with confinement in one dimension (perpendicular to the epitaxial grown layers). The ideal extension of these concepts would be to create a three-dimensional periodic array of nanoclusters. In the MBE and ALE synthesis of nanostructures, a two-dimensional layered substrate is used. Molecular sieves and zeolites are examples of possible three-dimensional substrates consisting of periodic crystalline porous frameworks with open channels and cages. They have extremely high-internal surface areas, as much as 800 cm^2/g and as high as 50% void space, so that high concentrations of nanoclusters and optical densities are possible. Clusters and molecules can be incorporated within these cages and channels either directly during synthesis, by "ship in the bottle" synthesis within the host, or by gas phase or melt inclusion into an empty host. The thermal stability of these frameworks depends on the framework composition, but in some cases it is over 1000° C.

A schematic illustrating the structural chemistry of some zeolites is shown in Figure 7. M in the empirical formula at the top of Figure 7 refers to a monovalent organic or inorganic cation. The framework is made up of AlO_2- and SiO_2 units which are connected so that the Al and Si atoms are tetrahedrally coordinated. By using organic molecules or inorganic cations as templates when these connections are made during synthesis, a large variety of channels and cages can be constructed. Figure 7 shows an example of condensation of the AlO_2^- and SiO_2 units into a 60 atom (silicon, aluminum, and oxygen atoms) sodalite cage which geometrically is a truncated octahedron. The upper right hand part of Figure 7 shows only the 24 metal atoms which make up the sodalite cage. The 36 connecting oxygen atoms connecting these metal atoms (middle figure, top of Figure 7) make up the remainder of the 60 atoms in the polyhedron.

The usual convention is to designate the pore openings by the metal atoms only. Thus, the term "6 ring" is used to describe the hexagonal faces shown for the sodalite cage in the

Figure 7.

Illustration of zeolite composition and synthesis. The 60 atom sodalite cage can be used to form "clusters of cages" in different ways to give the indicated zeolite structures.

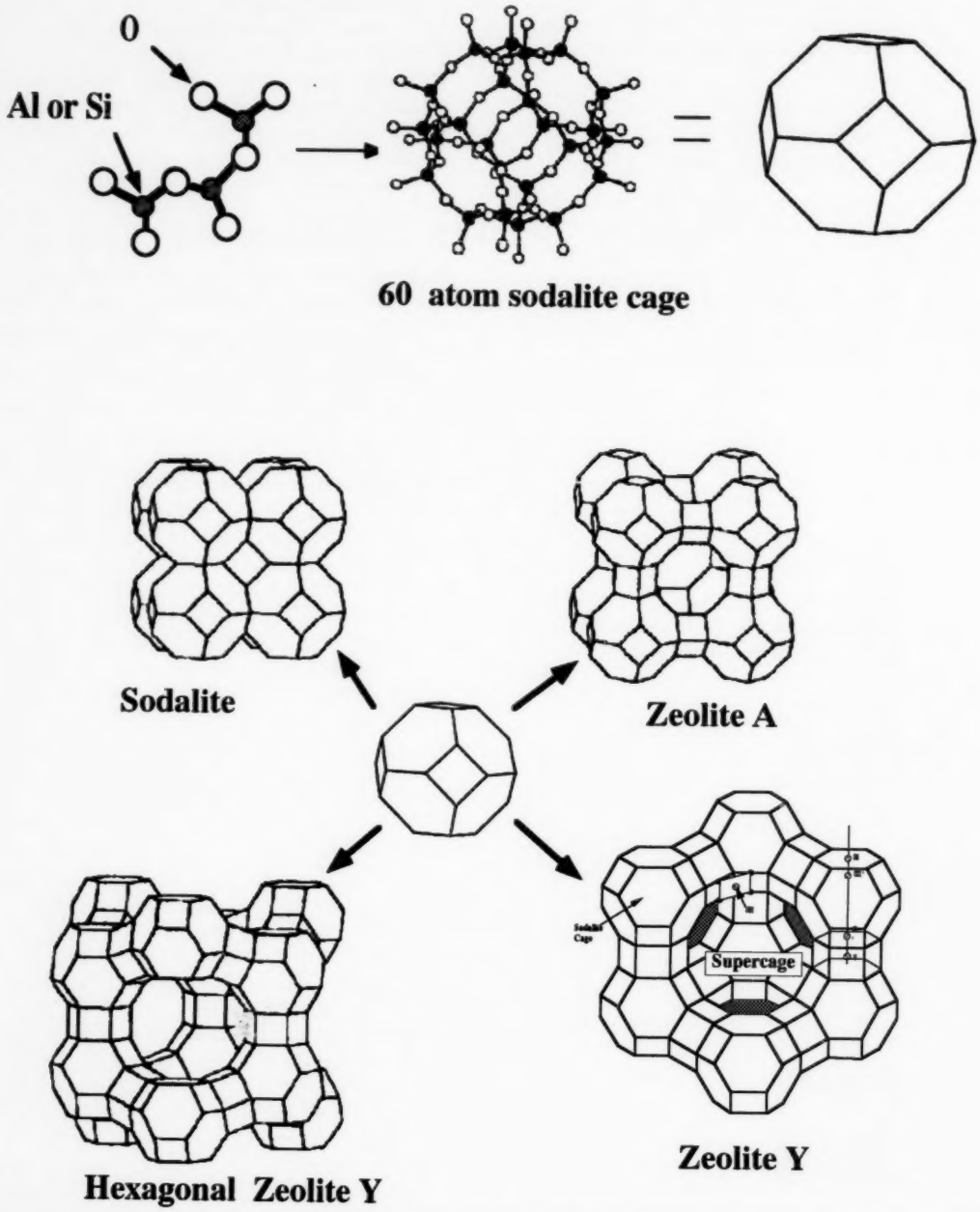
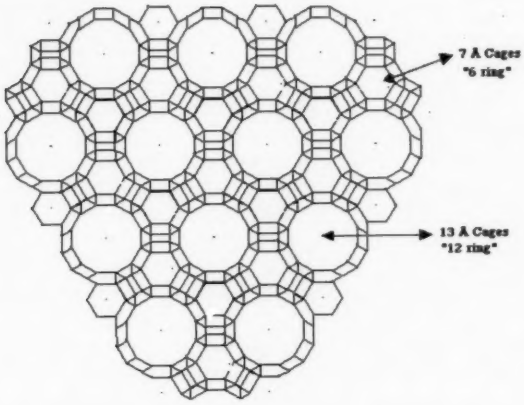


Figure 8.

Section of periodic 3-d lattice of zeolite Y.



upper right hand corner of Figure 7. The reader should be aware that these are in fact 12 atom ring openings with alternating metal and oxygen atoms. Similarly, the "4 rings" define 8 atom (metal + oxygen atoms) ring openings. In the remainder of this paper we will retain the usual zeolite molecular sieve convention of denoting these pores by the metal atoms only (i.e. as 6 rings and 4 rings).

This simple cage structure is an important fundamental building block and can be used to generate different porous zeolite structures by structural architecture based on putting together "clusters of cages" as shown in Figure 7 for sodalite, zeolite A, zeolite Y, and the hexagonal form of zeolite Y. In these structures, the oxygen atoms coordinated perpendicular to the surface of the truncated octahedron can be part of another cage (sodalite) or serve as connections to other cages (zeolite A and Y structures). The net result is a periodic, 3-dimensional crystalline lattice of cages and channels (Figure 8).

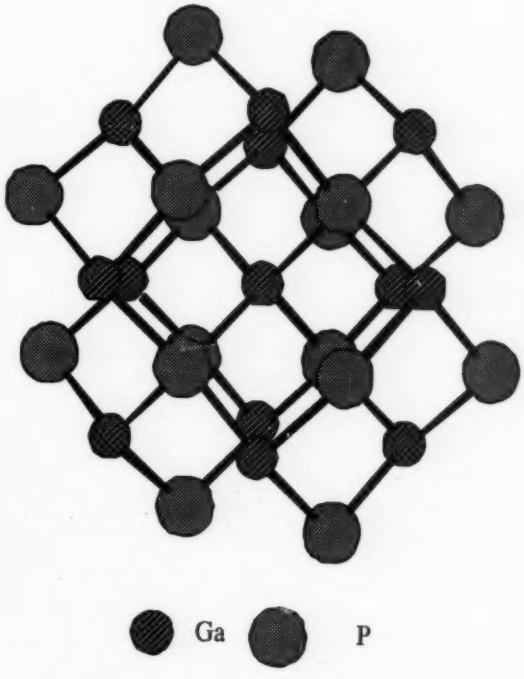
The inclusion chemistry of I-VII[36-38], II-VI[39-41] and III-V[42] semiconductors[43] has been investigated concentrating on the structural, optical, and photochemical[44,45] aspects of the clusters. The following discussion focuses on the formation of binary semiconductor systems in a superlattice host. Two roles of the superlattice host are emphasized: 1) the definition of the quantum confinement geometry, and 2) perhaps more importantly, the three- dimensional periodicity which directs the formation of a "supra-molecular" composition and the overall quantum lattice. Some examples of the use of selective siting and the use of host internal surface topology to define cluster geometry follow.

Zeolite Y, an aluminosilicate host, has two types of cages available for cluster formation, the smaller 6 Å sodalite units and the larger 13 Å alpha cages (Figure 7). For the purposes of this discussion there are 5 sites (I,I',II, II', III) which are available for cation siting within the sodalite and supercages. II-VI and I-VII quantum confined clusters can be synthesized by well understood ion-exchange methods, followed in the II-VI case by treatment with H_2S or H_2Se. It is important to note that the ion exchange process can yield very different siting of cations depending on temperature, pH, solvent vs. melt ion inclusion, other extra-framework ions, calcination, and loading levels. Thus, this process must be systematically controlled, along with the conditions for treatment with H_2S or H_2Se in order to obtain materials which can be consistently reproduced and which contain monosize clusters.

Structural studies by X-ray diffraction and EXAFS methods[46] have established cubane like clusters of $(CdS)_4$ located in the sodalite cages of the structure with each cadmium atom coordinated to three framework oxygen atoms and three S atoms. The framework fills the role of capping ligands described for the molecular clusters above. The sodalite cage acts

Figure 9.

$Ga_{16}P_{13}$ cluster synthesized in zeolite Y.



as a cluster templating agent which stabilizes the cubane like geometry. However, the clusters produced in this way are small compared to the volume available for formation of clusters in the supercages. For this reason, and also to study III-V semiconductors, a metal organic chemical vapor deposition (MOCVD) approach to the synthesis was used.

The reaction of $(CH_3)_3Ga$ with PH_3 carried out within the pores of the zeolite gives GaP_x particles which show blue shifts in the UV-V is spectra and upfield shifts in the solid-state NMR. Both these shifts are indicative of size quantization effects.[47] Extended X-ray absorption fine structure (EXAFS) spectroscopy has identified particles of ~11 Å in diameter, corresponding to 3 coordination spheres of the bulk structure (see Figure 8). X-ray diffraction data confirm long range ordering of the cluster electron density located in the supercages of the structure, but with different cluster orientations from cage to cage. This observation supports the EXAFS data for clusters which are close to the size of the diameter of the supercage.

The research in this area is rapidly gaining momentum.[47,48] Japanese scientists have systematically synthesized and studied semiconductor nanocomposites made up of selenium[49], tellurium and lead iodide clusters[50] within molecular sieve frameworks. The absorption band energies in these systems depend on the size of the cage or channels with energies which are considerably blue-shifted compared to the bulk exciton energies. Other researchers have studied tungsten oxide[51] and silver halide clusters and constructed supralattices of the semiconductor clusters by building them up from the isolated cluster and then gradually adding nearest neighbor cluster to determine intercluster effects.[52] Considerable exploratory work is still needed, however, in single crystal or thin film growth and in obtaining larger cages and channels. Considerable progress is being made in resolving both of these problems.

Summary

The understanding and new synthetic approaches to nanocluster synthesis have opened extensive new vistas for all areas of science. The incorporation of nanoclusters into composites will require the continued development of highly sophisticated new chemical techniques and molecular engineering. Much will depend on the ability to utilize and understand the exterior surface chemistry of the nanophsases. The health of the field has been demonstrated by rapid progress in optoelectronics and the recent isolation of large new polyhedral aromatic clusters, fullerenes. Control of cluster geometry and size distribution by the topography of three-dimensional host surfaces, makes it possible to create semiconductor quantum superlattices. The use of large three-dimensional surface areas permits concentration studies of cluster interactions over a wide range, and at relatively high-optical densities. It is to be expected that novel, normally very unstable, nanosized phases can be synthesized and stabilized via encapsulation and integration with the open polyhedral framework systems that are now being developed.

Biography

Galen Stucky received his Ph.D. in 1962 from Iowa State University in physical chemistry. After postdoctoral study at MIT in physics, he served as a faculty member in the Division of Inorganic Chemistry at the University of Illinois for 16 years (1964-1980). He has also held positions at Sandia National Laboratory (1979-1981) and DuPont Central Research and Development Department (1981-1985). He joined the UCSB chemistry faculty in 1985. Dr.Stucky has been particularly active in the American Chemical Society, serving as Editor of the Journal of Inorganic Chemistry for eight years, Chairman of the Solid State Subdivision, Chairman of the Inorganic Division and more recently a member of the Inorganic Division Executive Committee. He has served on the Advisory Boards of the Journals of *Inorganic Chemistry* and *Chemistry of Materials*. His recent research publications and interests cover a wide range of topics including the synthesis of new nonlinear optic materials, photoinduced superconductivity, 3-d packaging of electro-optic molecular and atomic arrays and low temperature materials synthesis.

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Special Clusters

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Making Clusters

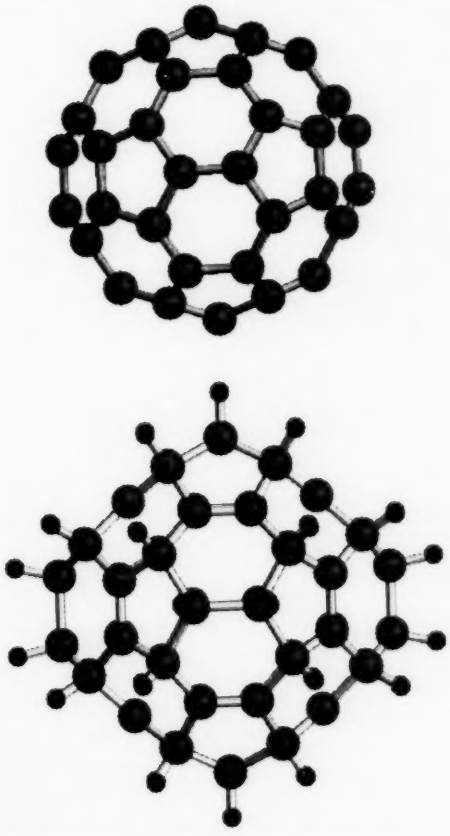
Researchers have long used beams of particles and/or laser light to bombard surfaces. In vacuum, this bombardment sputters away the surface and affords many techniques for studying the particles that are knocked out of the surface. In a good vacuum most of the particles that are sputtered away are electrically neutral and are individual atoms rather than clusters of atoms. The process of beam bombardment is violent enough, however, that atomic ions are emitted in sufficient abundance that a simple mass spectrometer becomes a powerful instrument for determining the elemental composition of almost any surface. More powerful mass spectrometers with higher resolution can be used directly to study the ionic clusters that are emitted in even lesser abundance. Slightly more sophisticated methods, such as crossing the plume of sputtered material with a beam of electrons, allows the study of the neutral atoms and clusters that are emitted. The principal limitation of this direct method of studying surfaces is the volatility of the bulk material whose surface one wants to study. The vapor pressure of the material itself or other gases above the surface clearly can affect the transport of material from the surface if the pressure is sufficiently high. The manipulation of the pressure above the surface and the bombarding beam has contributed significantly to a new science, cluster science, that is already producing new chemicals.

The bombardment process is so violent that one can imagine that all the different particles that can be made form the bulk material would be made. Such a view is supported by the fact that positive and negative as well as neutral atoms and clusters are emitted from almost any surface if the energy density of the beam is high enough. One might think that this would be a poor approach to making new chemicals because a statistical problem arises. Updating the old story of monkeys typing at random on typewriters thereby producing a Shakespearean play: One could easily have a supercomputer write huge numbers of manuscripts at random. No one does this because no one would be willing to wade though all the nonsense in the search of something useful. In the case of clusters, this statistical problem is less formidable than in the case of manuscripts, because automated techniques for sorting chemicals are much more developed than are automated techniques for sorting manuscripts. Nevertheless, the statistical problem of chemicals from clusters is still formidable.

If one assumes that a cluster source produces some amount of all the possible chemicals that can be made from the elements composing the beam and its target, then the source would produce only an infinitesimal fraction of any particular desired chemical. If all the unwanted material were thrown away, then the chemical of interest would be very expensive in terms of the amount of starting material required. Alternatively, if the unwanted material was recycled, then it would be expensive in terms of its energy content. Luckily, at the Naval Research Laboratory (NRL) an important discovery was made while a new high-performance mass spectrometer was being calibrated. Researchers discovered that certain clus-

Figure 1

The C_{60} cluster in its special Buckminsterfullerene structure (top) which can now be readily produced in macroscopic amounts. The first product that has been synthesized from it is $C_{60}H_{36}$ (bottom), which is made by hydrogenating 36 of the 60 carbon atoms comprising the original highly conjugated molecule. This figure was made by Daniel Robertson using the Application Visualization System on a Stardent GS 2025 graphics computer.



ters are more abundant than other clusters despite the violence the sputtering process.[1] While analyzing spectra form the alkali halides, an example of which is ordinary table salt (sodium chloride), they found that the abundant clusters formed a regular series. In particular the abundant clusters from table salt were not clusters of either sodium or chlorine, the two elements that together in equal numbers form table salt, but were ultrafine granules of salt itself—submicroscopic versions of the much larger cubic salt crystals in a shaker. This discovery was of no immediate value, because sputtering is a very expensive way to pulverize salt; but it did show that certain "magic" species could be made in abundance in cluster sources. This discovery also showed that the problem of isomerization, different chemicals having the same elemental composition and molecular weight, was not overwhelming.[2] Since then many different "magic-number" clusters have been found.

So far, one of these magic-number clusters, C60, has led to the production of large amounts of a number of related new chemicals that cannot yet be made by conventional synthetic means. Conventional synthetic means can, however, transform these new chemicals into still more new chemicals. This leads to the very technologically important question, what other types of new chemicals might one expect to see made by violent process such a sputtering in the not too distant future? To put this question onto perspective it is worthwhile to review the C60 story.

C_{60}

The most important "magic-number" cluster found so far is C_{60}, which was discovered and probed in various ways by several experimental research groups. Most of these experiments used laser vaporization cluster sources, which are easier to control than heavy particle beam sources. Kroto, Smalley and coworkers[3] related the enhanced abundance of C_{60} to the quite symmetric soccerball structure, buckminsterfullerene, displayed at the top of Fig. 1. This molecule is a highly conjugated form of carbon, like graphite, but has a large first electronic excitation.[4] Many unusual properties stem from and contribute to its high stability. One is its high ionization potential. That ionization potential can be measured by seeding the region above the laser vaporization process with a gas of known ionization potential and seeing whether or not a charge transfer reaction will occur between C_{60}^+ ion and the seeded gas. By this method, work at NRL[5] has determined that the ionization potential of C_{60} is approximately half an electron volt higher than either C_{58} or C_{62}. (One of the not fully resolved questions of cluster science is why only clusters containing an even number of carbon atoms are usually produced for cluster sizes larger than C_{30}.)

The spherical soccer-ball structure of C_{60} is formed by 12 pentagonal five-atoms rings of carbon uniformly distributed over its surface. The pentagons are separated by twenty hexagonal six-atom graphitic rings, which in the absence of the pentagonal rings could lie in a plane as a portion of single sheet of graphite. This highly symmetric molecule has not yet been synthesized using conventional techniques from organic chemistry. It has the highest point-group symmetry possible, icosahedral. The closest that conventional methods have come in making quite symmetric portion of this molecule is $C_{20}H_{10}$ (corranulene),[6] which has a five-fold subsymmetry (C_{5v}) of the icosahedral group. The bottom of the bowl-shaped corranulene molecule is formed by a pentagon of carbon

atoms. The pentagon is connected to five sets of hexagonal carbon atoms is completed by the twenty hydrogen atoms.

Icosahedral C_{60} is a remarkable stable structure. Using an empirical hydrocarbon potential developed at NRL,[7] studies of its scattering from a hard surface, hydrogen-terminated diamond, and a soft surface, graphite, are in progress.[8,9] C_{60} bounces, quite like one might expect given its soccerball structure. It reacts very weakly with either surface. Given high enough impact energy (above 200 eV), sufficient internal energy can be given to the departing C_{60} to fragment it eventually. These and other estimates suggest that is takes over twenty electron volts of internal energy to fragment the molecule.

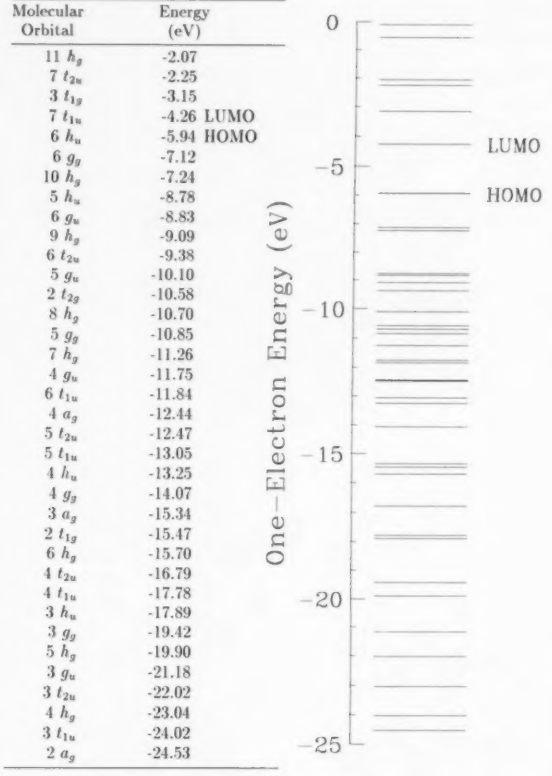
For this particularly stable molecule, varying the gas pressure over the graphite surface during laser vaporization dramatically affects relative proportion of C_{60} that is produced.[3] This effect is so large that macroscopic amounts of C_{60} can be produced in an atmosphere of about 100 torr of helium[10] using an extremely simplified version of the sputtering process outlined above. A high current of electrons is driven across a very small gap between two carbon electrodes much as it is done in carbon arc lamps. This current erodes the surfaces, and the emitted atoms and clusters recombine in the helium atmosphere making copious amounts of C_{60} together with smaller amounts of related fullerenes such as C_{70}. The structure of C_{70} is similar to that of C_{60}, but with an additional ring of hexagons around an equator. Recently this method has been refined to yield 14 percent of these two molecules, and a method has been developed to separate them.[11]

Despite the fact that C_{60} is such a stable molecule, its atoms are to a good approximation sp^2 coordinated, and thus the molecule is highly conjugated. Powerful methods from conventional organic chemistry exist to hydrogenate conjugated double bonds. Using such methods $C_{60}H_{36}$ has been synthesized.[12] It is shown at the bottom of Fig. 1. The 24 carbon atoms are not hydrogenated and 36 atoms are. The electronic structure (one-electron energy levels) of C_{60} using local-density-functional methods developed at NRL is shown in Figure 2 and compared to that of $C_{60}H_{36}$ in Figure 3.[13] Both molecules are quite stable because of the large difference in one-electron energy between the highest occupied molecular orbital (HOMO) and the lowest occupied molecular orbital (LUMO). The HOMO's for C_{60} and $C_{60}H_{36}$ are -5.9 and -4.9 eV respectively. The LUMO's for C_{60} and $C_{60}H_{36}$ are -4.3 and -1.2 eV respectively. To a first approximation the optical spectra of these molecules correspond to exciting an electron from an occupied orbital below the LUMO to an unoccupied level above the HOMO (subject to the appropriate selection rules, e.g. parity considerations require that *g* orbitals only be excited to *u* orbitals and *vice versa*). The energies of these excitations are underestimated by a factor of approximately 1/3 by simply subtracting the two appropriate one-electron energies at this level of approximation. More sophisticated local-density-functional calculations produce photoelectron

Figure 2

The density functional valence electronic structure of C_{60}. The numerical one-electron energies are given to the left in the figure and this information is displayed graphically to the right.

Molecular Orbital	Energy (eV)	
11 h_g	-2.07	
7 t_{2u}	-2.25	
3 t_{1g}	-3.15	
7 t_{1u}	-4.26	LUMO
6 h_u	-5.94	HOMO
6 g_g	-7.12	
10 h_g	-7.24	
5 h_u	-8.78	
6 g_u	-8.83	
9 h_g	-9.09	
6 t_{2u}	-9.38	
5 g_u	-10.10	
2 t_{2g}	-10.58	
8 h_g	-10.70	
5 g_g	-10.85	
7 h_g	-11.26	
4 g_u	-11.75	
6 t_{1u}	-11.84	
4 a_g	-12.44	
5 t_{2u}	-12.47	
5 t_{1u}	-13.05	
4 h_u	-13.25	
4 g_g	-14.07	
3 a_g	-15.34	
2 t_{1g}	-15.47	
6 h_g	-15.70	
4 t_{2u}	-16.79	
4 t_{1u}	-17.78	
3 h_u	-17.89	
3 g_g	-19.42	
5 h_g	-19.90	
3 g_u	-21.18	
3 t_{2u}	-22.02	
4 h_g	-23.04	
3 t_{1u}	-24.02	
2 a_g	-24.53	



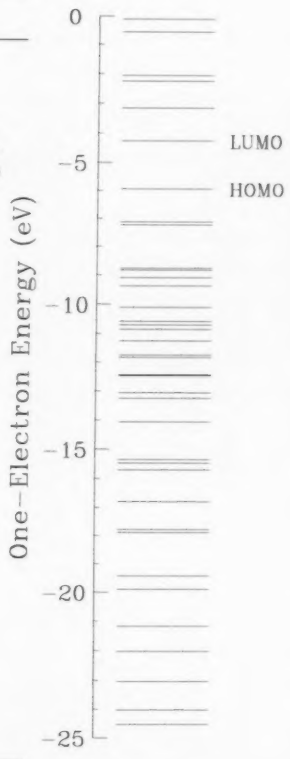
spectra and cross-sections that agree with experiment of C_{60} and have predicted the spectra for the other two currently available fullerene materials C_{70} and C_{84}.[14]

This first demonstration that chemistry can be done with C_{60} makes the creation of many new chemicals and polymers from this basic building block almost a certainty. An obvious next goal would be to hydrogenated the remaining 24 carbon atoms to make $C_{60}H_{60}$ in which every carbon atom is four-fold coordinated. Total energy empirical-potential and density-functional calculations suggest that this is possible, but the hydrogen atoms are bound less strongly in $C_{60}H_{60}$ than in $C_{60}H_{36}$. A more rewarding synthesis effort may be to try to make $C_{60}F_{60}$.[15] Finally, starting with C_{60} unusual routes to new chemicals may be possible. Very recent work at NRL has

Figure 3.

The density functional valence electronic structure of $C_{60}H_{36}$, as in Figure 1. (The relatively low symmetry of this molecule precludes listing to the left all the valence levels that are plotted to the right.)

Molecular Orbital	Energy (eV)	
29 t_u	-0.04	
12 e_g	-0.13	
12 a_g	-0.39	
28 t_u	-0.58	
23 t_g	-0.63	
7 a_u	-1.15	LUMO
27 t_u	-4.90	HOMO
22 t_g	-5.21	
11 e_g	-5.45	
26 t_u	-5.69	
11 a_g	-5.75	
6 e_u	-7.09	
21 t_g	-7.15	
25 t_u	-7.33	
6 a_u	-7.38	
24 t_u	-7.39	
10 e_g	-7.43	
20 t_g	-7.46	
10 a_g	-8.14	
19 t_g	-8.29	
23 t_u	-8.41	
9 e_g	-8.67	
5 a_u	-8.78	
18 t_g	-8.79	
22 t_u	-9.04	
5 e_u	-9.06	
21 t_u	-9.43	
17 t_g	-9.50	
16 t_g	-9.68	
8 e_g	-9.79	
20 t_u	-10.15	
19 t_u	-10.30	
9 a_g	-10.63	
15 t_g	-10.98	
18 t_u	-11.30	
14 t_g	-11.36	



shown that collisions can force a helium atom into C_{60} without knocking carbon atoms directly out of the cage itself.[16]

Other Special Clusters

The potential for new materials from cluster sources is great. The biggest challenge is to make the desired clusters in high abundance. That challenge is least severe for "magic-number" species that are especially stable, such as the alkali-halide clusters that are ionically bound together in cubes, and buckminsterfullerene that is covalently bound into a spherical shells. The spherical shell nature of the fullerenes is very helpful in eliminating isomers that might compete in the production of the special isomer. The numbers of ways that atoms can be arranged on the surface of a sphere is orders of magnitude smaller than the ways that they could be arranged in a solid three-dimensional cluster. The number of ways that atoms can be arranged on the surface of a sphere is formidable nevertheless. Restricting attention to the fullerenes where every atoms is three-fold coordinated on the surface, the enumeration problem reduces to that of finding the number of ways that 12 pentagons and 20 hexagons can be arranged to full the surface. For C_{60} that number is 1790,[17] which is not a small number. The extra stability of C_{60} in the truncated icosahedral arrangement is apparently sufficient to make its creation dominant over the 1789 other potential C_{60} fullerenes that might have been created.

If one adds to the 1790 fullerenes possible C_{60} clusters that have some four-fold coordinated carbon atoms such as occur in diamond and saturated hydrocarbon then the number of possible C_{60} clusters becomes astronomical. Given all these potential C_{60} clusters, it is truly remarkable, and thus likely to be of great technological importance, that special high energy processes can pick out the truncated icosahedral C_{60} isomer. In addition to cluster structure there is another variable that further enriches the potential for obtaining new chemicals from cluster sources. This additional variable, which is possessed by certain atoms, is an internal magnetic moment that can point in an arbitrary direction. Thus the number of different clusters that can be made from iron, nickel, and cobalt atoms, for example, is very large indeed. One might think that these additional degrees of freedom would preclude the possibility of special magnetic clusters that could be produced in large quantity by laser vaporization or other high-energy methods. One fact, however, suggests that this might not be the case.

Magnetism is caused by near degeneracy in the orbital energies of electrons, which are required by the Pauli principle to have unique orbitals with individual energies. The point-group symmetry of a cluster can force an additional amount of degeneracy on the energies of the electrons. Of all the symmetries that three-dimensional clusters could have, icosahedral symmetry can add the most additional degeneracy by forcing five electrons to have the same energy. Studies of 13-atom iron[18] and nickel[19] clusters show that as a rule icosahedral clusters are more magnetic than clusters having lower symmetry. Furthermore, alloying iron clusters with other elements, while constraining the entire cluster to have icosahedral symmetry, can enhance this effect. Altering the central atom of 13-atom iron cluster can increase the magnetic moment of the unalloyed cluster by over 20%.[20,21]

Another property of all icosahedral clusters is that they tend to be quite round, like C_{60}, because they must be invariant under all 120 operations of the icosahedral group. Thus icosahedral magnetic clusters can be both round and have high magnetic moment. Both properties could aid in developing

high energy methods for creating special magnetic clusters. The enhanced magnetic moment alone would make such clusters valuable in practical applications.

A byproduct of the separation of C_{60} are several other related molecules including C_{70}. Thus it is possible that methods could be developed to recover significant amounts of related but less special clusters once methods have been developed to extract the most abundant cluster produced using a given starting material and background pressure. If a sufficient number of successful methods are devised for extracting these less special clusters, then, among numerous other benefits, producing macroscopic amounts of special magnetic clusters would become a real possibility.

Biography

Brett I. Dunlap is a staff member in the Theoretical Chemical Section of the Chemistry Division of the Naval Research Laboratory, where he and coworkers have pioneered in the development of total energy density functional methods for chemistry. These methods are sufficiently developed that they are presently an ideal first-principles theoretical tool for studying these large special clusters. These methods are the basis of the program DGauss within the Unichem system of programs available from Cray Research, Inc.

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Research Notes

Higher Fullerenes and Cluster/Surface Interactions

Professor Robert Whetten at UCLA has been involved in carbon cluster research from the beginning of the field and recently has made several significant advances in understanding fullerene structures and properties. For example, he, with an interdisciplinary group of scientists, have led the way in the production, extraction and purification of fullerenes larger than C_{60} and C_{70}. Specifically, large amounts of C_{76}, C_{78} and C_{84} have been produced and this allowed characterization of many properties, including elucidation of isomeric and chiral structures. Secondly, he has developed the first instrumental method in which cluster/surface interactions can be investigated in a controlled and systematic manner. With his technique, clusters can be selected according to size and energy, collided with a well-characterized surface and the scattered species or the surface can then be analyzed. One example of his work is the finding that unlike other clusters or molecules, C_{60} when collided with a surface at high energy does not fragment to any significant extent, revealing yet another unique property of this unusual and new form of carbon; resiliency. In general, his studies have revealed new insights into how clusters (C_x, Si_x and alkali halide clusters) interact with surfaces (HOPG, Si), which is crucial information if clusters are to be used, in one of the many potential applications, as precursors for thin films.

Fullerene Chemistry at NRL

The experimental research effort on cluster chemistry at the Naval Research Laboratory has focused recently on fullerene properties. For instance, using Fourier transform mass spectrometric techniques, Dr. Stephen McElvany has determined several properties of gas-phase fullerene molecules, including first, second and third ionization potentials, ion/molecule reactivity and proton affinities. Study of the last property yielded the discovery that not only does C_{60} have a proton affinity higher than that of ammonia but also that the $C_{60}H^+$ species is very stable. This finding has important relevance to the speculation that such a fullerene species might be responsible for some of the unidentified diffuse interstellar bands. Secondly, Dr. John Callahan (with M. Ross) provided the first, unambiguous evidence of the formation of an endohedral complex of C_{60}^+ and He via gas-phase, kilovolt collisions. Supported by corroborative molecular dynamics simulations of the He/C_{60}^+ collisions by Dr. Richard Mowrey, several important insights were gained into this unprecedented behavior, including He trapping probability as a function of collision energy and trajectory. These studies are yielding new information on fullerene stabilities and reaction chemistry.

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